PHD

The application of ultrasound to phosphazene chemistry

Harrison, Stephen

Award date:
1996

Awarding institution:
University of Bath

THE APPLICATION OF ULTRASOUND TO PHOSPHAZENE CHEMISTRY

submitted by Stephen Harrison
for the degree of PhD
of the University of Bath
1996

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

AKNOWLEDGEMENTS

I would like to thank Dr.'s G J Price, K C Molloy and B J Brisdon for their help, guidance and support throughout this PhD.

Thanks too, to those at DRA Fort Halstead for their help, encouragement and financial support, notably Dr. E. Colclough.

To all of those people in the lab. who have made life bearable, even when everything seemed to be going wrong (Ian, Emma, Andy, Pete, Tom and Simon) - Thank you!

Last but not least, Mam, Dad and Claire I don't say this very often, but thanks for your encouragement in everything I've chosen to do - it means a lot!

SUMMARY

The work described in this thesis extends previous knowledge of substitution patterns in phosphazenes, reports novel substituted phosphazenes capable of further reaction and is the first reported investigation of the potential applications of ultrasound in phosphazene chemistry.

A series of substitution reactions of hexachlorocyclotriphosphazene have been carried out and a number of complicating side reactions identified as well as the reaction prodcts aimed for. Ultrasound has been applied to a selection of these substitution reactions of hexachlorocyclotriphosphazene and compared to the conventional reactions. The results indicate that ultrasound may be of some use in promoting higher levels of substitution in these reactions and may prove to be a useful tool in solving some of the many mechanistic problems encountered in reactions with these materials.

Several polymerisation reactions of hexachlorocyclotriphosphazene have been investigated with the intention of applying ultrasound in order to gain greater control over the properties of the polymer obtained. This was found to be impractical with the equipment currently available. An initial study of the ultrasonic polymerisation of alkoxy substituted phosphinimines has been carried out, with the result that polymers with some of the lowest polydispersities reported for polyphosphazenes have been formed. The use of ultrasound has also been found to result in the formation of polymers with a higher molar mass than those formed in the corresponding conventional polymerisation reactions.

A study of the potential of ultrasound to tailor the properties of preformed polyphosphazenes by degradation has been carried out with the effects of ultrasonic intensity and polymer solution concentration having been looked at. The polyphosphazenes have been shown to behave in the expected manner based upon literature reports of the ultrasonic degradation of a number of other polymer systems. The applicability of a number of kinetic models for ultrasonic degradation to this system has been looked at and it has been concluded that none provide a good description of the degradation investigated, although some basic trends can be deduced from this work.

Some potential applications of these findings have been suggested along with proposals for further studies in this area.

CHAPTER 1

INTRODUCTION

This thesis will describe work into the effect of ultrasound on an inorganic polymer system (polyphosphazenes). In order for the various methods used and ideas presented to be appreciated fully, some general background material will be described first. This will include some general polymer chemistry, a description of the development and diversity of phosphazene chemistry (which will include some non-polymer chemistry, as much of the work carried out in this project was at the small molecule level) and finally some background into the theory and applications of ultrasound.

1.0 INTRODUCTION TO POLYMERS

A polymer may be defined as a material which is composed of molecules which have long sequences of one, or more, types of atom, or groups of atoms, linked to each other, usually by covalent bonds. A polymer is formed by the linking together of monomer molecules through chemical reaction and may be linear or non-linear (branched or cross-linked) and can be derived from many or only one type of monomer. (Figure 1.0)

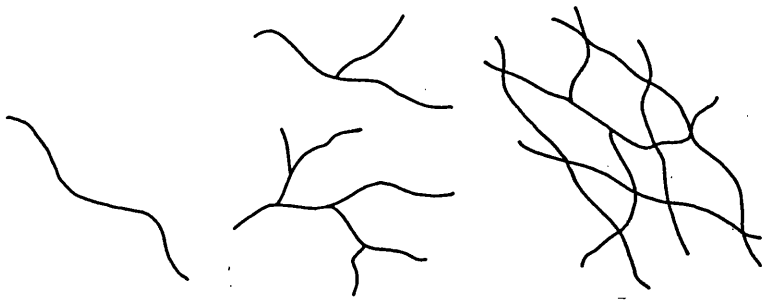


Figure 1.0 Diagram of linear, branched and cross-linked polymers

Homopolymers are polymers which are derived from one type of repeat unit.

~A-A-A-A-A-A-A~ = -$[A]_n$-

Copolymers are polymers which are derived from more than one type of repeat unit and which may have these repeat units arranged in a number of possible ways;
- i) A polymer in which the distribution of repeat units follows known statistical laws is known as a STATISTICAL COPOLYMER.
- ii) A polymer in which the distribution of repeat units is completely random is known as a RANDOM COPOLYMER.

~~B-B-A-B-A-A-A-B-B-B-A~~

- iii) When two different repeat units are arranged alternately along the polymer chain the polymer is known as an ALTERNATING COPOLYMER.

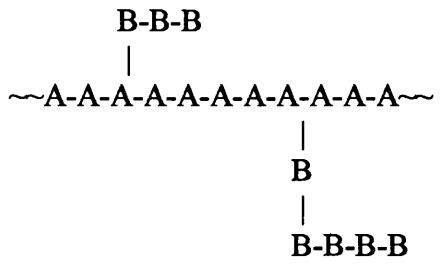
~~A-B-A-B-A-B-A-B-A-B-A~~

- iv) Polymers in which the repeat units are arranged in long sequences of the same type are known as BLOCK COPOLYMERS.

~~A-A-A-A-A-A-B-B-B-B-B~~ AB diblock copolymer

~~A-A-A-A-B-B-B-B-A-A-A~~ ABA triblock copolymer

- v) A branched polymer in which the branches have a different chemical structure to that of the main chain is known as a GRAFT COPOLYMER.



Polymers may be further classified according to their physical behaviour, for example, THERMOPLASTICS are linear or branched , homo- or copolymers which are highly coiled and tangled macromolecules. Upon the application of heat they decrease in viscosity and may be moulded and remoulded into virtually any shape. ELASTOMERS are lightly cross-linked polymers which may be stretched easily and which rapidly regain their original dimensions when any applied stress is released. THERMOSETS are highly cross-linked molecules in which chain motion is greatly restricted and so are generally rigid materials and which cannot be reversibly melted.

Polymers have a vast array of applications, the majority of which are encountered in everyday life and which range from electrical and high temperature insulators (e.g. wire coatings and pan handles), fabrics (e.g. nylon and Terylene), various packaging foams (e.g. polystyrene) to aeroplane windows (Perspex). Even chewing gum consists of a polymeric material.

It can be seen that polymers make up a very important part of our lifestyles and so it is vital that as much as possible is known about both their chemical and physical properties.

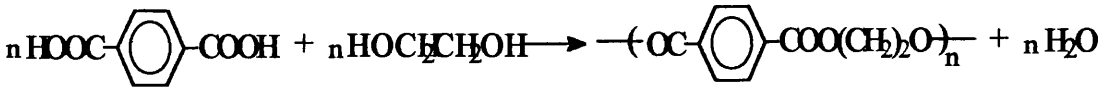
1.1 SYNTHESIS OF POLYMERS

There are a great many different chemical reactions which lead to polymers. However, most polymerisations may be classed as one of two types, either STEP-GROWTH or CHAIN-GROWTH, based on the underlying polymerisation mechanisms.

1.1.1 STEP-GROWTH POLYMERISATION

Step-growth is the formation of polymer chains through successive reactions which couple monomer units together to form dimers, which may then react with other dimers or with further unreacted monomer units. It is characterised by a rapid monomer consumption along with a gradual growth of polymer chains.

An example of a polymerisation type with a step-growth mechanism is CONDENSATION POLYMERISATION - a reaction between an organic acid and an organic base in which a small molecule is eliminated, for example, the synthesis of poly(ethylene terephthalate) (PET) from terephthalic acid and ethylene glycol



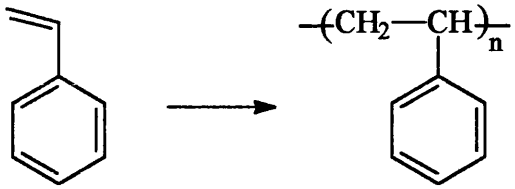
1.1.2 CHAIN-GROWTH POLYMERISATION

Chain-growth is the formation of polymers by the addition of one monomer unit to the growing chain at a time. It is characterised by the consumption of monomer units along with the presence of long polymer chains at an early stage in the reaction. Chain-growth polymerisation generally has three distinct steps, initiation, propagation and termination.

Examples of polymerisation types with chain-growth mechanisms are FREE-RADICAL and IONIC POLYMERISATION. Both are used in the polymerisation of

vinyl monomers with free-radical polymerisation being the most widely practised method of chain-growth polymerisation.

For example, the polymerisation of vinyl chloride to poly(vinyl chloride) (PVC) or of styrene to polystyrene.



Under the correct conditions certain anionic polymerisations can become what are known as LIVING POLYMERISATIONS, in which the propagating cationic chains permanently retain their active centres and continue to grow so long as monomer is available, since no termination mechanisms exist.

1.2 CHARACTERISATION OF POLYMERS

Before being considered for application purposes as much as possible must be known about the physical and chemical properties of a polymer. For example, the temperature range within which a polymer is stable and any transitions which may occur within that range as well as what effect various solvents may have on the behaviour of the polymer need to be known.

1.2.1 MOLAR MASS AVERAGES

Because a polymer sample generally consists of molecules with a range of different molar masses, it is convenient to characterise its distribution in terms of molar mass averages. Since the molar mass of a polymer changes in steps of M_0, where M_0 is the molar mass of a monomer unit, the distribution is actually discontinuous (although these discontinuities are very small relative to the overall molar mass range) and the polymer molecules actually exist in discrete fractions. It is this which is used to define the various molar mass averages.[1]

Number average molar mass, M_n

The number average molar mass is the arithmetic mean of the molar mass distribution and is defined as the sum of the products of the molar mass of each fraction multiplied by it's mole fraction.

i..e. $\overline{M_n} = \sum \chi_i M_i$ where χ_i =mole fraction of molecules of molar mass M_i

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i}$$

Weight average molar mass, M_w

The weight average molar mass can be defined as the sum of the products of the molar mass of each fraction multiplied by its weight fraction.

i.e. $\overline{M_w} = \sum w_i M_i$

where w_i = the total mass of molecules of molar mass Mi divided by the total mass of all the molecules present.

since $w_i = \frac{N_i M_i}{\sum N_i M_i}$ it can be shown that $\sum\left(\frac{w_i}{M_i}\right) = \frac{\sum N_i}{\sum N_i M_i}$

hence;

$$\overline{M_n} = \frac{1}{\sum\left(\frac{w_i}{M_i}\right)} \quad \text{and} \quad \overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Polydispersity, γ

The polydispersity (or heterogeneity) is often used as a measure of the breadth of the molar mass distribution. It is the ratio of the weight average molar mass and the number average molar mass and is greater than unity for a polydisperse polymer sample. The larger the value of γ, the larger the range of molar masses in the sample.

i.e. $\gamma = \frac{\overline{M_w}}{\overline{M_n}}$

Other molar mass averages

Higher molar mass averages are sometimes quoted when specific measurement techniques are used, e.g. the z-average molar mass, often obtained from sedimentation equilibrium data, is defined as,

$$\overline{M_z} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i}$$

The viscosity average molecular weight can be obtained from dilute solution viscometry.

$$\overline{M_v} = \left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{\frac{1}{a}}$$

where *a* is a term which characterises the interactions between the polymer and a particular solvent.

The degree of polymerisation, X

For homopolymers the degree of polymerisation averages may be obtained simply by dividing the corresponding molar mass average by M_0, the molar mass of the monomer unit.

$$\overline{X_n} = \frac{\overline{M_n}}{M_o} \qquad \overline{X_w} = \frac{\overline{M_w}}{M_o}$$

1.2.2 THERMAL TRANSITIONS OF A POLYMER

The ranges in which the various mesophases of a liquid crystalline polymer exist are very important to the possible applications of that material. Similarly the temperature range in which an elastomer displays its rubbery properties needs to be known if that polymer is to be used effectively. Therefore it is vital that the various thermal transitions (e.g. melting point and the glass transition temperature) can be measured accurately.

1.2.3 STRUCTURAL FEATURES

The macromolecular structure of a polymer has a direct effect on such properties as the glass transition temperature, whether microcrystallinity is observed and numerous other important properties relating to their applications. It is therefore important that as much as possible is known about such things as the arrrangement of

monomer units in copolymers, the stereochemistry of side groups and the degree of branching on a polymer chain.

1.3 POLYMER CHARACTERISATION TECHNIQUES[1]

1.3.1 THE MOLAR MASS DISTRIBUTION

A variety of methods exist for determining the molar mass averages and the distribution of a polymer sample, among them end-group analysis, ultracentrifugation and the measurement of various colligative properties. However, the most common techniques used are solution viscometry, in which the effect of a dissolved polymer on the viscosity of a solvent is studied relative to the viscosity of the pure solvent. Solution viscometry is a very simple technique, however, it is a laborious and time consuming process due to its need for calibration.

Light scattering, an absolute technique, in which the intensity of light scattered by a solution of the polymer under investigation, is measured through a range of angles. If different concentrations of this polymer solution are studied a Zimm plot can be constructed and information such as the weight average molar mass and the mean square radius of gyration of the polymer sample may be extracted.

Gel Permeation Chromatography, GPC

GPC, developed during the mid 1960's,[2] provides polymer chemists with a quick and easy method for obtaining the molar mass distribution of a polymer sample. Typically, this can be obtained within an hour of beginning an analysis and it was for these reasons that GPC was used to determine the molar mass averages in this study.

GPC is a form of size-exclusion chromatography and a schematic diagram of some typical apparatus is shown in figure 1.3.1

High quality pumps which give accurately known, pulse free, constant flow-rates of solvent are essential. The solvent flows through one (or many) column(s) which are packed with beads containing a porous gel. These beads have a range of pore sizes and are typically cross-linked styrene-divinyl benzene copolymers for organic solvent systems or "Sephadex" for aqueous systems.

The detectors are usually non-destructive and measure the concentration of separated species by using differential refractometers or U.V. or I.R. photometers. The fact that they are non-destructive means that the various fractions of polymer may be collected if desired.

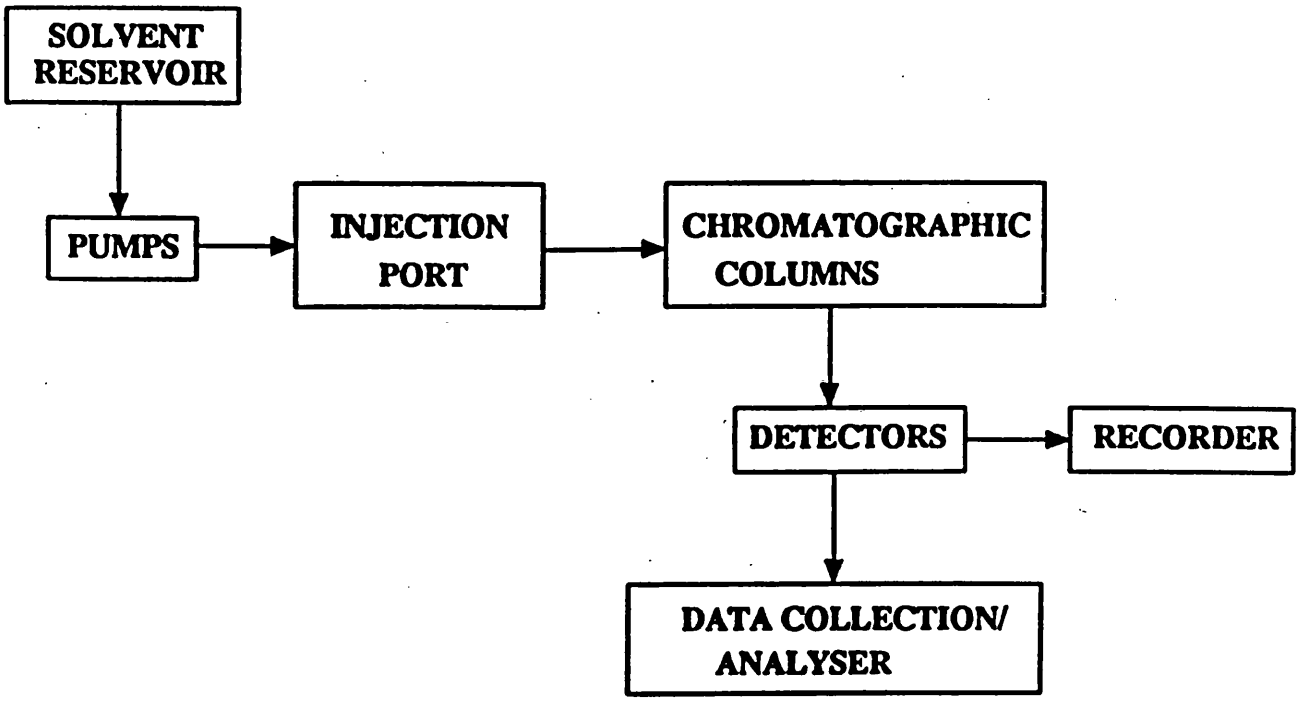


Figure 1.3.1 Schematic of GPC apparatus

Typically, a dilute solution (< 1%) of the polymer of interest is injected into the solvent stream which then flows through the column. The solvent molecules, carrying the polymer molecules, pass through and around the porous beads in the column. The smallest polymer molecules, able to pass through most of the pores in the beads, have a relatively long flow-path, whereas the larger molecules, excluded from all but the largest pores, have a short flow-path. As a result, the molecules are eluted from the column in order of decreasing molecular size in solution, and the chromatogram is obtained as a function of concentration vs. elution volume/time.

To convert the chromatogram into a molar mass distribution it is neccessary to know the relationship between molar mass and elution volume/time. This is obtained by the construction of a calibration plot.[3] Calibration curves are generally obtained from the use of one of two main methods:

- i) The retention times of standards with known and narrow molar mass distributions are measured [e.g. polystyrene, poly(methyl methacrylate) and poly(ethylene oxide) standards are commercially available] and a curve of log(M) vs. V_R is plotted. The problem with this technique is that it is essentially specific to the polymer under study and a calibration curve for each polymer on a given solvent / temperature / column system needs to be constructed.

- ii) A Universal Calibration, derived from the work of Benoit[4] can be used, which assumes that the molecular size of a chain behaving normally in solution can be represented by the hydrodynamic volume, which in turn is proportional to $[\eta]M$, where $[\eta]$ is the intrinsic viscosity and M is the molar mass.
A plot of $\log([\eta]M)$ vs. V_R is approximately linear and is the same for all polymers.

i.e. $$[\eta]_s M_s = [\eta]_u M_u$$

s refers to standard,
u refers to unknown

From the well known Mark - Houwink equation[1], $[\eta] = KM^{\alpha}$,

$$[\eta]_s M_s = K M_u^{1+\alpha}$$

hence, $$M_u = \left(\frac{[\eta]_s M_s}{K} \right)^{\frac{1}{1+\alpha}}$$

where K and α are the Mark - Houwink constants for the unknown polymer sample, under the conditions of the GPC analysis. The system is calibrated using readily available standards for which both K and α in the solvent used are known and from this, the calibration curve for almost any other polymer may be constructed, provided that K and α for that polymer are known. If K and α are not known it is possible to obtain them using GPC - Viscometry, in which RI and viscosity detectors are used in series.

Although the Universal Calibration is available, most workers tend to quote measured molar mass averages relative to a standard (usually polystyrene) and this is the procedure adopted in this thesis.

1.3.2 THERMAL TRANSITIONS

Both dilatometric (density measurement) and calorimetric (measurement of heat changes) techniques can be used to detect thermal transitions by measuring such things as the change in the volume of a material or the change in the specific heat of a material, although calorimetric techniques are by far the more usual.

Differential Thermal Analysis, DTA

In this technique the difference in temperature between a sample and a reference is measured as the temperature is raised by a common heating source.

Differential Scanning Calorimetry, DSC

A schematic of the apparatus used in DSC is shown (Figure 1.3.2),

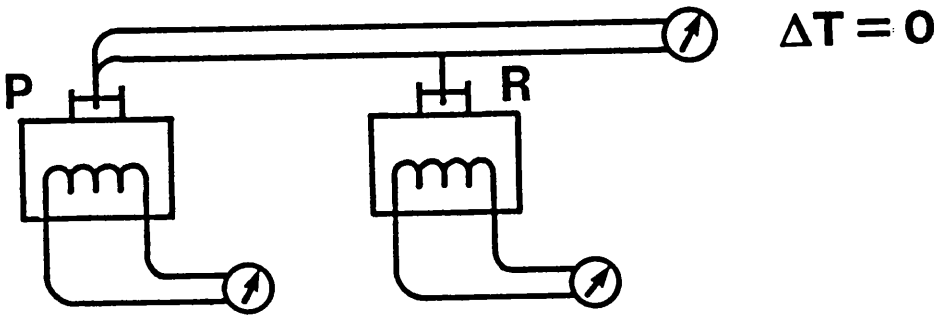


Figure 1.3.2 Schematic of DSC apparatus

The polymer and reference samples have seperate heating elements in which the currents flowing are adjusted so as to keep the temperature difference between them zero. As the temperature of the two samples is raised the differential power required to keep the temperature of the two the same is measured. (This is effectively measuring the rate of energy input vs. the sample temperature)

$$\frac{dH}{dT} \qquad \text{i.e. } Cp$$

A typical DSC trace is shown (Figure 1.3.3)

Differential Scanning Calorimetry was used to determine the thermal transitions of the polymers under study in this thesis.

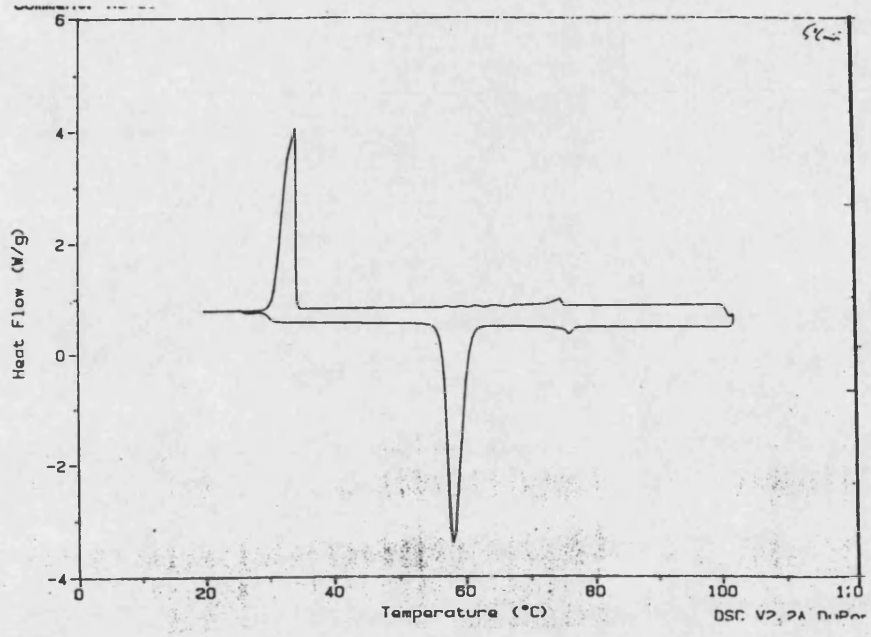


Figure 1.3.3 A typical DSC trace

1.3.3 STRUCTURAL FEATURES

As with any molecule the general structural features of a polymer may be determined using the well known applications of the various spectroscopic techniques (i.e. IR, UV and NMR). For example, the presence of functional groups and hence an estimation of the numbers of co-monomers is possible using IR and UV spectroscopies as is a determination of the degree of crystallinity in a polymer. NMR spectroscopy can be used to determine stereochemical structure in a polymer chain and also to find the chemical composition and the sequence distribution in copolymers.

A further technique, frequently used in polymer science, is Electron Spin Resonance spectroscopy, ESR, which can be used to detect free-radicals during cross-linking, photochemical degradation and mechanical fracture of polymers.

1.4 INORGANIC POLYMERS

Even with the vast number of organic polymers and copolymers available, with their huge array of properties and possibility for application, research is currently underway on discovering new and developing current alternatives, such as inorganic polymers. Why is this?

Most organic polymers consist of a compromise in properties rather than the ideal desired for application purposes. For example: many organic polymers react with

oxygen or ozone over a long period of time and many degrade when exposed to UV or γ-radiation. This means that problems may be encountered if the material is to be used out of doors. The fact that many organic polymers burn with the release of toxic fumes unless treated in some way is a problem well associated with the furniture industry , and the combination of few organic polymers degrading at acceptable rates in the biosphere as well as the continuously diminishing supplies of raw materials for their synthesis is also a cause for concern.

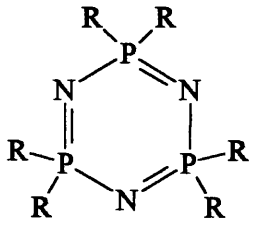
It is thought that by utilising inorganic polymers some, or all, of these problems may be avoided. In addition, the use of inorganic elements can generate different combinations of properties. Different valencies can result in differing numbers of side groups which can be attached to the polymer backbone, affecting such things as the flexibility of the molecule as well as interactions with other molecules such as solvents and chemical reagents. The bonds formed between inorganic elements are often stronger and more resistant to various types of cleavage (such as free-radical) and hence changes in bond angles and torsional mobilities can occur with the overall result of a change in material properties. A combination of the above means that the possibility exists of tailoring the chemical properties of a material in ways which couldn't be considered with organic polymers.

Currently most efforts are directed towards establishing the chemistry of inorganic polymers, however, in some areas, such as the polysiloxanes, various technological aspects are already well established.

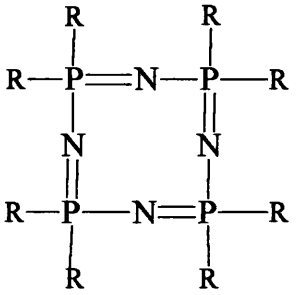
1.5 PHOSPHAZENES

Polyphosphazenes comprise one of the largest class of inorganic macromolecules studied to date, at least 300 different polymers of this type have been synthesised which have a range of properties that allow them to be used in such varied applications as solvent - resistant elastomers, flame - resistant, heat - , electrical - or sound - insulation materials and in biomedical uses such as drug delivery systems, hydrogels and membranes[5]. Different phosphazenes have such varying characteristics that they may be elastomers or glasses, water soluble or hydrophobic, they can be bioactive or completely bio-inert and either electrically conducting or insulating.

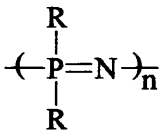
The phosphazene backbone consists of alternating phosphorus and nitrogen atoms with two side groups being attached to each phosphorus. The backbone may be cyclic (I, II) or linear (III), long or short and the side groups can be organic, organometallic or inorganic units.



(I)



(II)



(III)

As the overall final physical and chemical properties of phosphazenes depend on the nature of the side groups it is this potential for such a wide variety of substituents which gives rise to the large number of possible applications.

1.5.1 HISTORY OF PHOSPHAZENES

The origins of phosphazene chemistry can be traced back to the early 1800's to the observation by Wohler[6] and Rose[7] that phosphorus pentachloride reacts with ammonia to give a stable, white, crystalline solid. Over the next 50 years little interest existed in this product, however, it was concluded that its formula was $(NPCl_2)_3$ [8]. Initially it was believed that, in common with the reaction of PCl_5 with water to give $POCl_3$, the product was "$NPCl_2$", a monomer with a structure analogous to that of organic nitriles, and as such these materials were called *phosphonitriles* - a name which stuck even up to as recently as the late 1960's[9]. More recently these compounds have become known by the more common, trivial name *phosphazenes.*

The development of phosphazene chemistry can be divided into three main areas;

- i) 1800's to 1940's - The synthesis and main group inorganic chemistry of the halogenophosphazenes.

The basis of the commercial preparation of $(NPCl_2)_3$ was developed during this time and the basic hydrolysis, ammonolysis and aminolysis reactions were studied along with the reactions with alcohols and phenols. The beginnings of polyphosphazene chemistry can be traced back to this time with the discovery of "inorganic rubber" by H.N. Stokes at the turn of the century.[10] Due to the hydrophilicity of the material, however, this "inorganic rubber" was insoluble in all solvents due to cross linking during polymerisation. This resulted in only minor interest being demonstrated in the material until much later in the development of phosphazene chemistry.

- ii) 1940's to early 1970's - Studies of organic type, nucleophilic substitution reactions.

During this period aminolysis reactions were studied in particular detail[11], along with alcoholysis[12] and metathetical exchange[13] and various ideas about which parameters influenced the observed substitution patterns began to emerge.

- iii) Late 1970's onwards.

With the development of much more advanced analytical techniques such as NMR, UV, ESR and mass spectrometries, as well as crystallography, structural studies of phosphazenes became more accessible. The development of a synthesis for soluble poly(dichlorophosphazene)[14] resulted in an explosion of interest in this area and literally hundreds of different polyphosphazenes have been reported during this period. The organometallic chemistry of phosphazenes has also been a major research area during this time. Focusing on both main group and transition metals[15], work in this area has resulted in the observation of some of the most complex phosphazene chemistry yet seen, in which the course of the phosphazene reaction has been found to be dependent on the type of phosphazene being used, whether fluoro-, chloro-, bromo-, trimer, tetramer or high polymer as well as on the particular organometallic reagent being used.

1.5.2 BONDING AND ELECTRONIC STRUCTURE IN PHOSPHAZENES[16]

The electronic structure of cyclo- and polyphosphazenes has been a matter of some debate over the years, and as yet has not been fully resolved. When the general bonding characteristics of both nitrogen and phosphorus are considered it is generally accepted that a σ-bond framework can be built up in which the nitrogen atoms adopt an sp^2 hybridisation and the phosphorus atoms an sp^3 hybridisation.

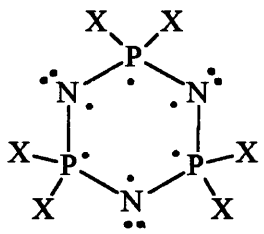


Figure 1.5.1. σ-bonding framework in cyclophosphazenes.

The result of this is that non-bonding, lone pairs of electrons at each nitrogen atom and one electron on each of the nitrogen and phosphorus atoms are

"unaccounted for". The generally accepted theory is that these electrons form some sort of π-bonding system.

Evidence for this π-bonding system includes various structural measurements, such as the observation that P-N bond distances in phosphazenes (generally in the range 1.47 - 1.62Å) are shorter than expected for pure, covalent, σ-bonds (1.77Å, from X-ray studies of sodium phosphoramidate).[17] Also, it is known that skeletal nitrogen atoms act as bases, especially when electron releasing ligands are attached to the phosphorus atoms.[18] However, it has also been observed that the normal spectral effects which signify organic, π-electron systems (such as a bathochromic UV shift with increasing delocalisation) are not associated with phosphazene systems.[14,19] Also, unlike organic aromatic systems, the phosphazene skeleton is difficult to reduce electrolytically.[20]

All of the available evidence points to the fact that phosphazene bonding is more than just a σ–bond framework, however, any π-system present is unlike the σ–π bond systems in aromatic organic species. How is the π-bonding system constructed?

Stable phosphorus compounds can contain phosphorus atoms which are bound from 3 to 6 other atoms. For coordination numbers of four and higher, the suggestion has been made that the phosphorus 3d orbitals may participate in bonding. The existence of stable penta- and hexacoordinated compounds, such as PF_5, and PF_6^-, which are believed to contain sp^3d and sp^3d^2 hybrid orbitals respectively,[19,21] and back-bonding through a dπ-pπ coordinate π-bond, believed to be responsible for the observed phosphorus-carbon bond shortening when tetracoordinate phosphorus is bound to tricoordinate carbon,[23] is evidence that the 3d orbitals may participate in bonding.

However, evidence can also be provided to show that d-orbitals do not participate in bonding,[24] such as the fact that the higher coordinate phosphorus compounds are found with the most electronegative ligands, suggesting that ionic resonance forms may exist instead of sp^3d hybridisation. No proof can be gleaned from various physical techniques[25] (e.g. ^{31}P NMR, ESR and UV spectroscopies), for the involvement of d-orbitals, as the data is ambiguous.

All of this means that, in terms of phosphorus-nitrogen chemistry at least, the concept of 3d orbital contributions must be taken as unproved. However, the idea of a σ-framework accompanied by dπ-pπ bonds in phosphazenes provides the most satisfactory working model for the understanding of the electronic structure of these compounds.

Two models have emerged for the dπ-pπ bonding system. The first, that of Craig and Paddock,[26] suggests that the $3d_{xz}$ orbital on each phosphorus atom overlaps with the $2p_z$ orbital on adjacent nitrogen atoms.

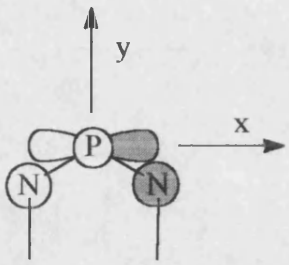


Figure 1.5.2. Craig and Paddock model of phosphazene bonding.

However, as a result of the gerade symmetry of the d-orbital, an eventual mismatch in the sign of the wavefunction is encountered as this model is applied around the ring, the resulting node would reduce the stability of the delocalised molecular orbital. It could be envisaged that the d_{yz} orbital would also be able to participate and thus, inherent in the argument of Craig and Paddock, is the assumption that the electronegativities of the d_{xz} and d_{yz} orbitals are not equal. This would mean that they do not contribute equally to the π-bond.

The model of Dewar, Lucken and Whitehead,[27] although similar to that of Craig and Paddock, states that no good reason exists for a difference in electronegativities between the d_{xz} and d_{yz} orbitals, and that both should contribute equally to the π-bond. The overall result is a hybridisation of the d_{xz} and d_{yz} orbitals to give orientation towards the nitrogen atoms.

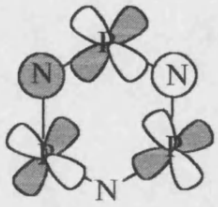


Figure 1.5.3. Dewar et al model of phosphazene bonding.

The π-molecular orbitals are now arranged in such a way that the skeletal delocalisation is interrupted at each phosphorus atom and 3-centre, "island" type bonds are formed.

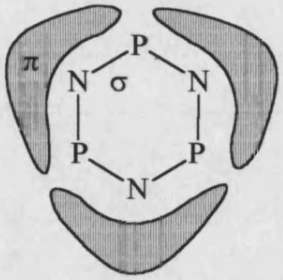


Figure 1.5.4. The "island" model of phosphazene bonding.

The possibility of an in-plane π' bond also exists by the donation of the lone pair of electrons on nitrogen to a $d_{x^2-y^2}$ orbital on phosphorus.

Neither of these two theories has been proved to the exclusion of the other and a summary of the experimental data supporting the models is given in a review by Mitchell,[24] however, the current general concensus of opinion tends to favour the "island" model of Dewar.

1.6 CYCLOPHOSPHAZENES

Both low and high molecular weight cyclic phosphazenes are known, indeed species with up to 40 repeat units have been detected,[28] but by far the most common and widely studied is the trimer, $(NPCl_2)_3$. This is mainly due to the fact that it is the easiest to synthesise (it is now commercially available) and that it easily undergoes many substitution reactions. It is used largely as a model for high polymer systems,[29] as reactions that work well at the cyclic level tend also to work well at the polymeric level. However, it has to be realised that the use of cyclophosphazenes as models for linear poly(phosphazenes) is essentially a compromise between an ideal model and experimental constraints.

1.6.1 SYNTHESIS OF HALOCYCLOPHOSPHAZENES

The reaction of ammonium chloride with phosphorus pentachloride is the most commonly used synthesis of chlorocyclotriphosphazenes.[30]

$$n\,NH_4Cl + nPCl_5 \longrightarrow (NPCl_2)_{3-10} + 4nHCl \qquad (2)$$

However, it is not the only method available,[31] the reaction of ammonium halides with halophosphoranes[32] and a synthesis via azide intermediates[33] being two other possibilities. Fractional distillation, extraction from petroleum by concentrated

sulphuric acid and sublimation under reduced pressure are just a few of the methods which have been used to isolate the various oligomers.

Analogous bromo- compounds can be made in a similar manner with the additional presence of Br_2 to suppress the decomposition of PBr_5.[34]

$$PBr_5 + NH_4Br \xrightarrow{\text{xs. } Br_2} (NPBr_2)_n \qquad (3)$$

Fluorocyclophosphazenes are prepared by metathetical exchange with chlorophosphazenes.[35]

$$(NPCl_2)_3 + 2nNaF \longrightarrow (NPF_2)_3 + 2nNaCl \qquad (4)$$

As yet, no synthesis for iodophosphazenes is known.

1.6.2 REACTIONS OF HALOCYCLOPHOSPHAZENES

Of the various reactions known: (nucleophilic substitution, ring cleavage and polymerisation) it is probably nucleophilic substitution which could be considered to be the most important, as it is this which provides access to the vast multitude of different phosphazene compounds known. Although almost all of the materials used in applications are polymeric, in order for them to be useful they need to undergo nucleophilic substitution of some form.

Different types of halophosphazenes react differently. For example, tetramers are more prone to ring cleavage reactions than are trimers, fluorophosphazenes often react more simply than chlorophosphazenes, but, usually require harsher conditions to effect transformations [eg. $(NPCl_2)_3$ polymerises at 250°C whereas $(NPF_2)_3$ polymerises at 350°C].[36]

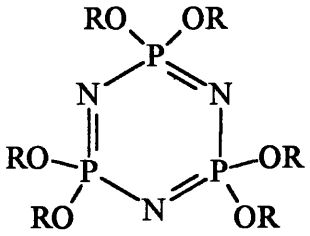
Some of the earliest studies into the reactions of cyclophosphazenes[37] looked at hydrolysis, ammonolysis and aminolysis reactions. Although complicated by further steps, all of these reactions showed initial substitution of the chlorine atoms prior to any subsequent reaction.

$$[NPCl_2]_n \xrightarrow{H_2O} [NP(OH)_2]_n \xrightarrow{H_2O} nH_3PO_4 + nNH_3 + nHCl \qquad (5)$$

$$[NPCl_2]_n \xrightarrow{NH_3} [NP(NH_2)_2]_n \longrightarrow [(NPNH)n] \longrightarrow (P_3N_5)n \qquad (6)$$

$$[NPCl_2]_3 + 12RNH_2 \longrightarrow [NP(NHR)_2]_3 + 6RNH_2.HCl \qquad (7)$$

The first hexa-alkoxycyclotriphosphazenes (IV) were prepared in 1949 by Dishon[38] from the use of methanolic sodium methoxide and n-butanol - pyridine mixtures.



(IV)

R = Me or n-Bu

The two methods used for the preparation of hexaalkoxy- and hexaaryloxyphosphazenes used by Dishon, (i) reaction with sodium alkoxides and aryloxides and (ii) reaction with an alcohol-pyridine mixture, were also investigated by Fitzsimmons and Shaw[39] and from their results they concluded that method (i) was preferred for the preparation of aryloxyphosphazenes and method (ii) for the preparation of alkoxyphosphazenes as it eliminated the need to prepare the sodium alkoxide.

Later studies into all manner of nucleophilic substitutions of halocyclophosphazenes attempted to unravel the factors which affected the observed substitution patterns. Up until about 1961 it was assumed that replacement of chlorine in hexachlorocyclotriphosphazene occured in geminal pairs,[37], but, the isolation of products in which one, or three[40] chlorine atoms had been replaced [e.g. $P_3N_3Cl_3(NEt_2)_3$][41] disproved the universality of pairwise replacement. It was also proposed[42] that in some systems one chlorine atom on each phosphorus atom is replaced successively and the second chlorine atom of a pair is only replaced when no geminal dichloro groups are left.

It has also been suggested[43] that as one chlorine atom is replaced, the other on the same phosphorus atom becomes labilised and hence easier to substitute.

Upon consideration of the possible substitution products available (figure 1.6.1) and the range of substituents possible, it would be expected that the factors deciding the regio- and stereoselectivity, beyond the level of monosubstitution, would include steric, electronic and possibly mechanistic effects and indeed all of these various influences are observed.[44]

Steric effects

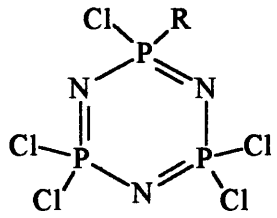
The size of any substituent already present, as well as the size of the incoming nucleophile, both play a part and large substituents tend to promote trans, non-geminal pathways, for example in $N_3P_3Cl_{6-n}(OC_6H_4Me\text{-}4)_n$,[45] as well as limiting the extent to which substitution can occur in extreme cases.[11,46] However, other factors may be strong enough to predominate over any steric effects, it has been observed that in reactions with primary amines, for example, that the pathway shifts from non-geminal to geminal with increasing steric bulk of the amine. This is clearly contrasteric and is due to competition between two reaction mechanisms.[47]

Electronic / Charge distribution effects

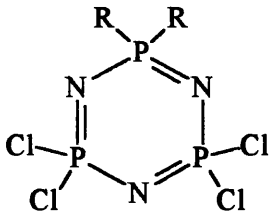
The type of substituent already on the phosphazene ring plays an important role in determining where any successive substitution will occur. Depending upon whether it is an electron donor or electron withdrawer and on whether this is σ or π electron oriented, the type of product can change.

Electron donors - π donors (e.g. aminide ions and oxyanions) tend to promote non-geminal pathways. This is due to a relative negative charge on the substituted phosphorus in comparison to the others.[48] Indirect evidence for this is observed in the reaction of $(NPCl_2)_3$ with aziridine,[49] in which the lack of exocyclic lone pair donation to phosphorus results in the loss of non-geminal substitution. The same is observed with pyrazoyl[50] and imidazoyl[51] derivatives. σ-Donors (e.g. thiolates) tend to promote geminal pathways as endocyclic lone pairs are directed towards unsubstituted centres leaving the PCl(R) site with a relative positive charge.[52] For example, $N_3P_3X_{6-n}(SR)_n$ where R = Et for n = 1 - 6, or Ph for n = 2, 4 or 6.
Direction by σ electron donation can, however, be surpassed by sufficiently large steric effects, as can be seen with some large organic substituents. e.g. with n-butyllithium and methyllithium, $N_3P_3F_6$ gives yields of the geminal, disubstituted derivative whereas t-butyllithium with $N_3P_3F_6$ gives good yields of the trans $N_3P_3F_{6-n}(t\text{-}C_4H_9)_n$ (n = 2, 3) derivatives.[53]

Electron withdrawers - (e.g. fluorine) tend to promote geminal substitution as a relative positive charge is induced on the substituted phosphorus atom.

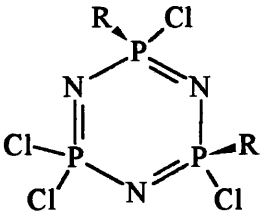


Monosubstituted



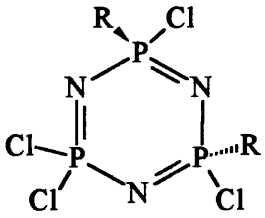
Bisubstituted

Geminal

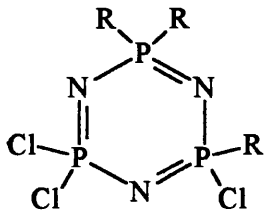


Non-geminal

Cis

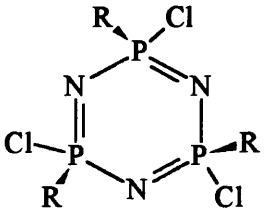


Trans



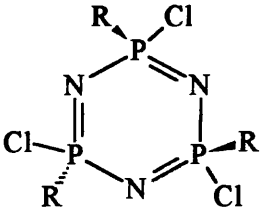
Trisubstituted

Geminal

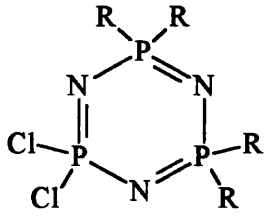


Non-geminal

Cis

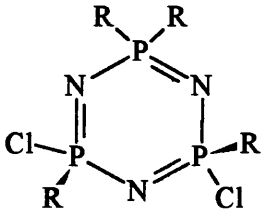


Trans



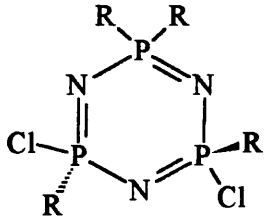
Tetrasubstituted

Geminal

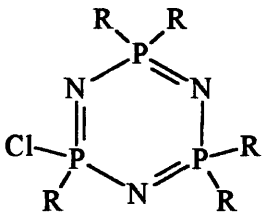


Non-geminal

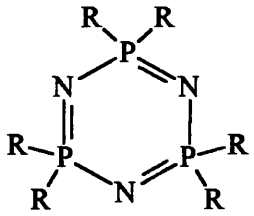
Cis



Trans



Pentasubstituted



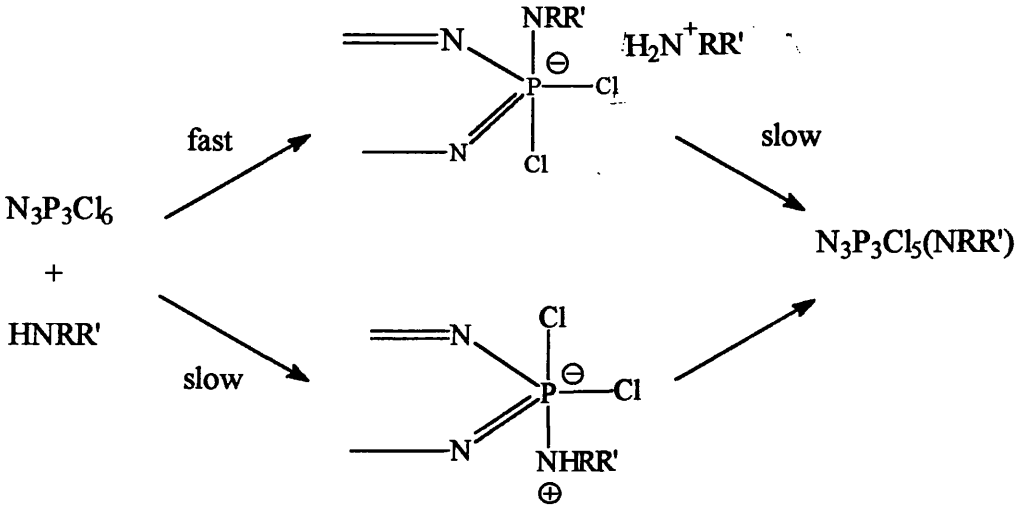
Hexasubstituted

Figure 1.6.1. Possible substitution patterns in cyclotriphosphazenes.

Mechanistic effects

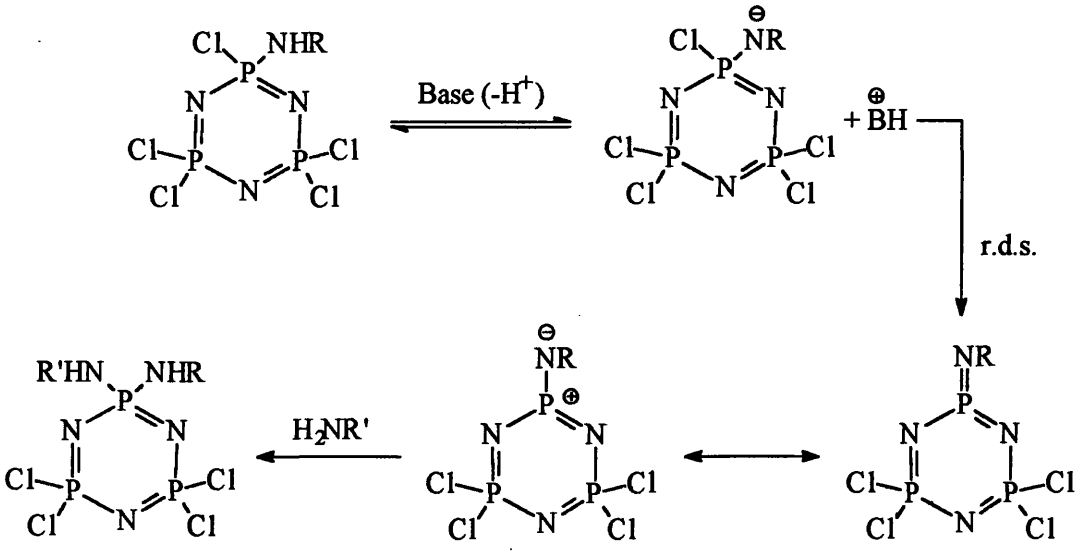
Phenomena observed in various systems have included the competition between two different mechanisms and solvent effects involved therein, electronic interactions between unsaturated moities and various side reactions. For example, the competition between a bimolecular and a dissociative mechanism decides the regioselectivity in reactions with amines.[47] The bimolecular mechanism has two possible pathways:

Scheme 1.6.1.



The dissociative mechanism :

Scheme 1.6.2.



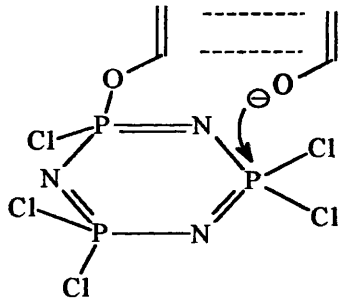
Smaller, primary amines are believed to follow the bimolecular mechanism which results in the incoming group being directed to the most accessible phosphorus

atom (an unsubstituted phosphorus due to electron donation to the substituted phosphorus and some steric influences) and non-geminal substitution occurs. For larger amines, the dissociative mechanism is favoured because of steric factors limiting their ability to take part in a bimolecular mechanism. The result is geminal substitution.

Solvent effects are also noticed in aminolysis reactions[41, 47, 55] as polar solvents favour the concerted, bimolecular mechanism (and hence non-geminal products) whereas the dissociative mechanism is more favourable in the generally less polar organic solvents.

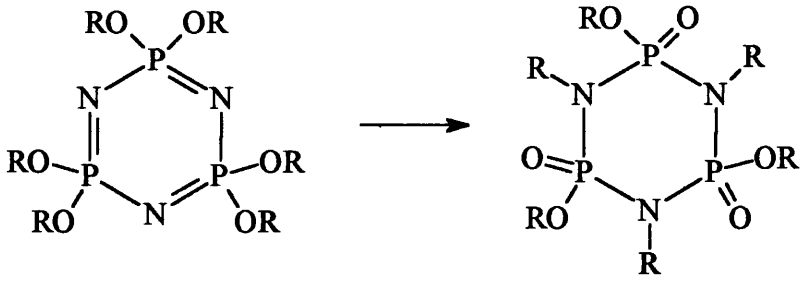
Substitution by vinyl groups tends to follow a cis, non-geminal pathway rather than the expected / usual trans, non-geminal path (a bimolecular mechanism is understood to be in effect).[56] The reason for this observed difference is believed to be due to interactions between the unsaturated vinyloxy group already attached to the strongly electron withdrawing phosphazene ring and the electron rich, incoming nucleophile.[57] This is shown in scheme 1.6.3.

Scheme 1.6.3.



Product distribution can also be affected by various side reactions and rearrangements.[58] For example, the involvement of ethereal solvents in Grignard mediated reactions is known to result in the formation of alkoxyphosphazenes due to "ether cleavage".[59] In non-geminal products cis - trans isomerisation is possible and is known to be promoted by various materials, among them, aluminium chloride, hydrogen halides and bases.[60] As amine hydrochloride is a side product of the reaction of chlorophosphazenes with amines, care must be taken when considering product distribution in these systems. Thermal tautomerisation of alkoxyphosphazenes to give alkoxyphosphazanes (V) is known.[61]

Scheme 1.6.4.



(IV) (V)

Even more complex reaction pathways have been observed in the most recent area of study in the reactions of phosphazenes, that of their organometallic chemistry.

Arising initially in the early 1970's and becoming much more widely / intensively studied in later years this area looks at the reactions of phosphazenes with both main group and transition metal reagents. It has been found that, in reactions with main group organometallic reagents, the type of phosphazene in the reaction is very important. For example, $(NPF_2)_3$ reacts with methyl-, n-butyl- or cyclohexyllithium reagents to give mainly monosubstituted products whose configuration depends on the size of the alkyl group.[62,53] With aryllithium reagents the overall transformations at the cyclic, trimer level are:

$$(NPF_2)_3 \xrightarrow[(-LiF)]{ArLi} N_3P_3F_{6-n}Ar_n \qquad (8)$$

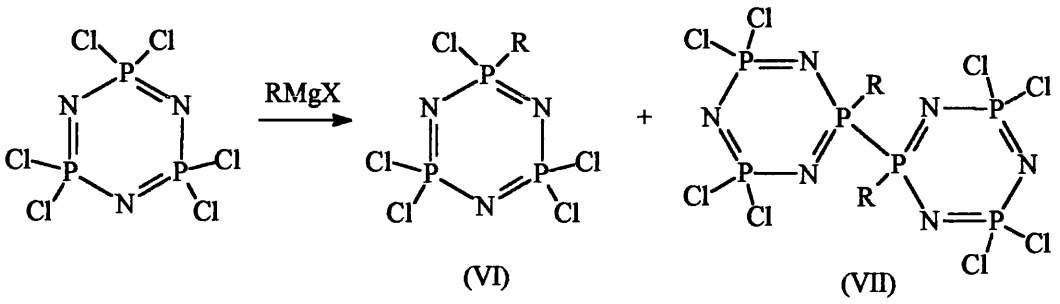
where n = 1 or 2 generally, but, by using a combination of aryllithium and Friedel-Crafts reactions,[63] has been raised to 4.

Chlorophosphazenes react differently, even to such an extent that simple organolithium compounds appear to be unsuitable reagents for substitution of chlorine by organic groups in $(NPCl_2)_3$. For example, with methyl- or phenyllithium, ring cleavage products predominate, although some traces of methylcyclophosphazenes have been isolated.[64] With methyllithium it is also thought that metal-halogen exchange occurs with the reaction proceeding through anionic intermediates, as a hydridophosphazene has been isolated as the major product in THF at -20°C.[65]

The main reason for the differences observed between the reactions of fluoro- and chlorophosphazenes is that of the relative electronegativities of fluorine and chlorine. The more electronegative fluorine is more able to strengthen the phosphazene skeletal bonds, probably by causing a contraction of the phosphorus d-orbitals, thus increasing their overlap efficiency.

Cyclic trimers are known to react differently to cyclic tetramers with a variety of different alkyl and aryl Grignard reagents. $(NPCl_2)_3$ reacts with RMgX to yield cyclic substitution products, the principal ones being the monosubstituted trimer and the bi(cyclophosphazene), a ring linked product.[66]

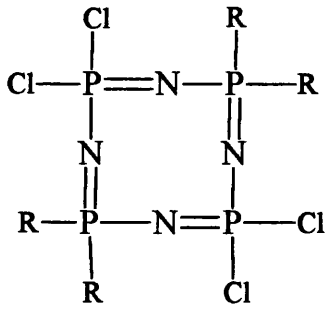
Scheme 1.6.5.



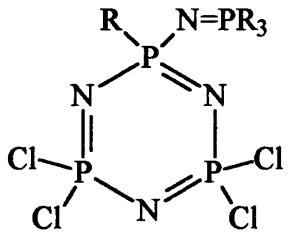
(VI) (VII)

The relative proportions of these two compounds is dependent on the size of R in the Grignard reagent.

The reaction of $(NPCl_2)_4$ with RMgX results in both substitution and ring cleavage[67] giving reaction products of the type shown below (II), (VIII) and (IX):



(VIII)

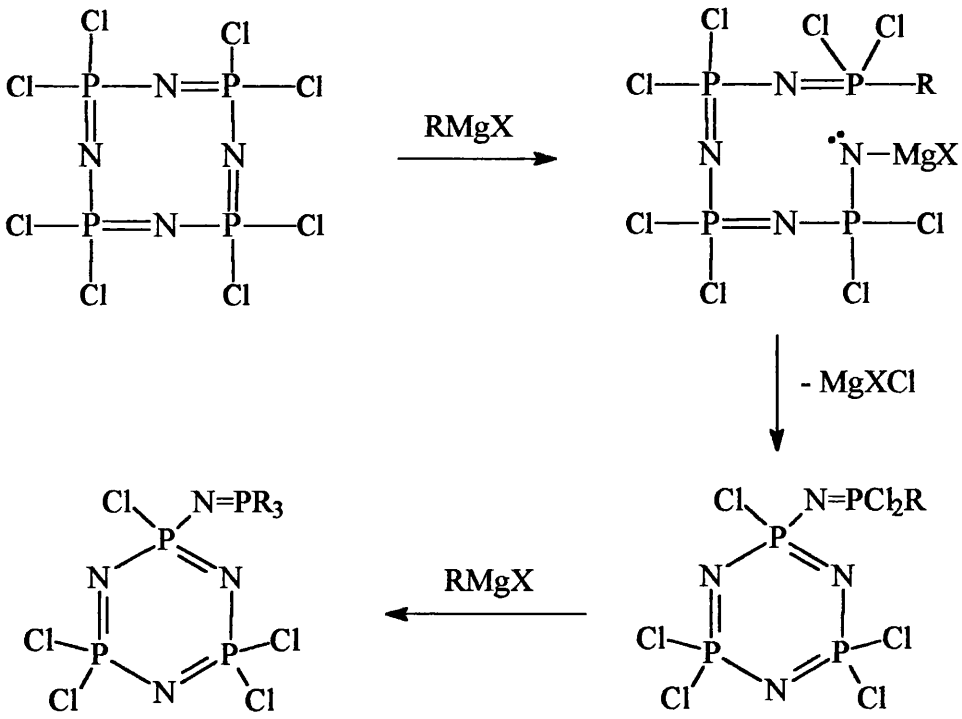


(IX)

The reasons for these differences appear to be mechanistic. In the reaction involving trimer a metal halogen exchange pathway is believed to be in operation, rather than the expected nucleophilic substitution.(Section 3.1.3)

The reaction of the tetramer involves ring cleavage in the initial interaction with RMgX, followed by 1,6 intramolecular nucleophilic displacement. Replacement of the chlorine atoms on the resulting side group then gives:

Scheme 1.6.6.



In reactions with transition metal organometallic reagents the products observed are more dependent on the type of reagent used and on the mode of linkage of the transition metal.

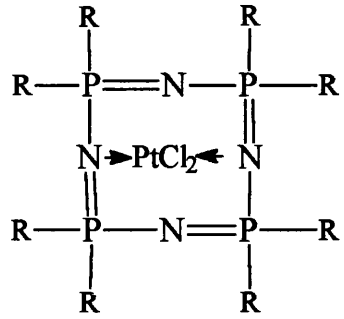
There are four general methods of attaching a transition metal to a phosphazene.

- i) By making use of the free electrons on skeletal nitrogen atoms.

Each skeletal nitrogen atom in the chain has a lone pair of electrons not involved in ring bonding that are available for coordination (see figure 1.5.1).

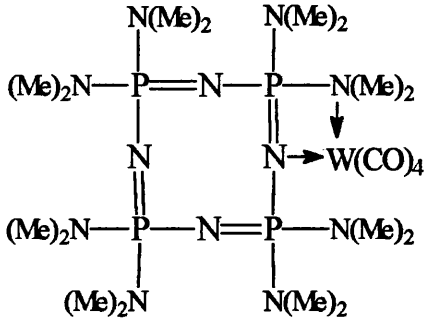
The availability of each pair of electrons is dependent on the nature of the side group X. Electron withdrawing groups reduce the basicity of the skeletal nitrogen, whereas electron donating groups enhance this basicity and make the binding of such things as protons,[68,69] alkyl cations[70] and transition metals possible. Among the types of systems known with this mode of linkage are metal halide complexes, for example, Allcock et al.[71] found that in the presence of 18-crown-6-ether, K_2PtCl_4 reacts with various aminophosphazenes to give compounds such as (X).

The high polymeric equivalent to this cyclic compound has been shown to act as a water soluble, anti-cancer agent which has restricted transmission through semi-permeable membranes. This reduces damage to the kidneys as the complex passes through the body.[71]



(X)

Metal carbonyl complexes are also known (XI), although they are not as well characterised as the metal halide complexes.[72]



(XI)

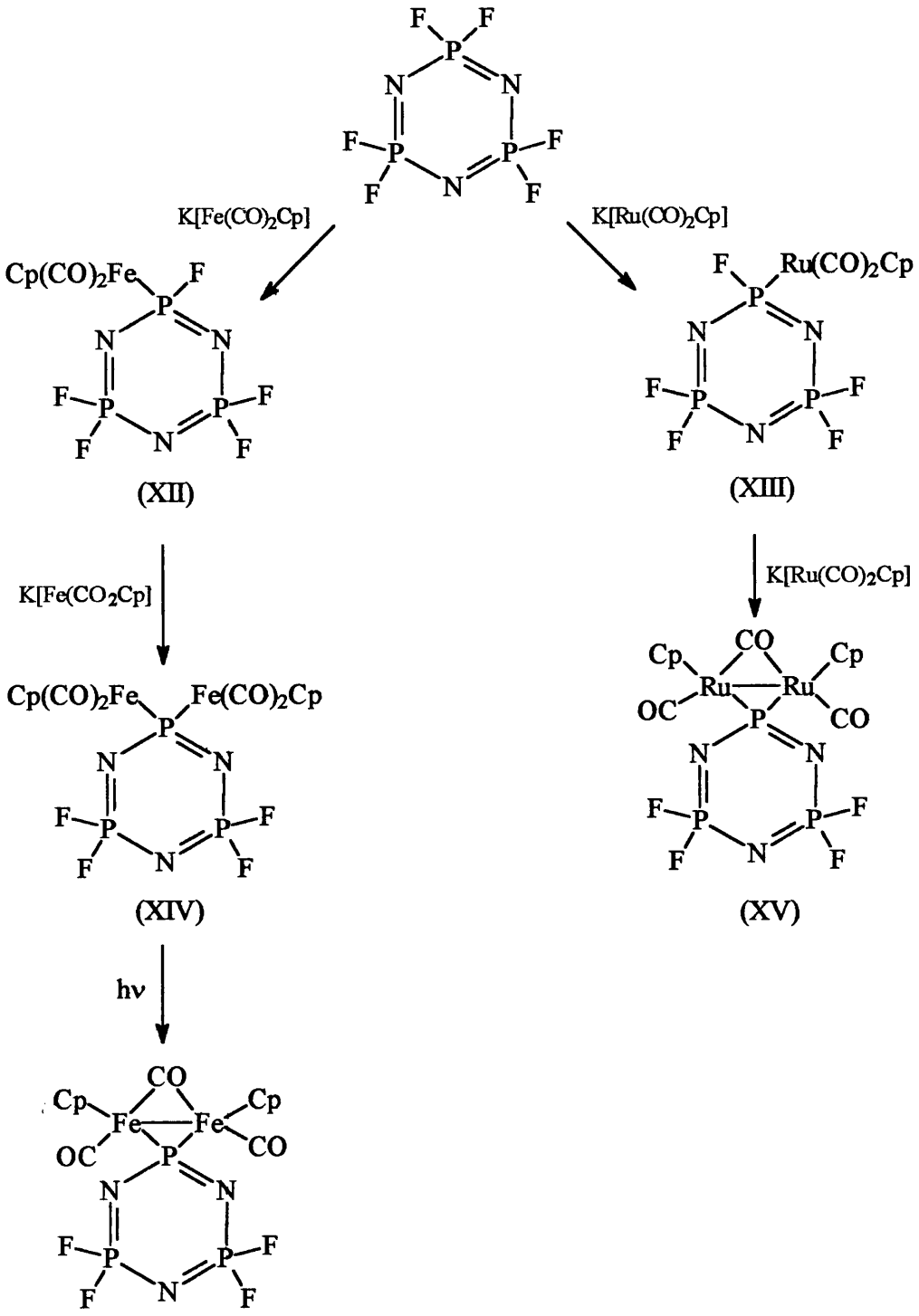
- ii) Ionic, salt type species

Amino- and alkylphosphazenes may aquire a proton or alkyl cation on the skeletal nitrogen atom to generate onium type sites. These sites can act as counterions for metallo-anions. For example, $[(NPMe_2)_4H]_2^+[CoCl_4]^{2-}$ [73] and $[HN_3P_3(NMe_2)_6]_2^+[Mo_6O_{19}]^{2-}$ [74] are known.

- iii) Metal - phosphorus covalent bonding.

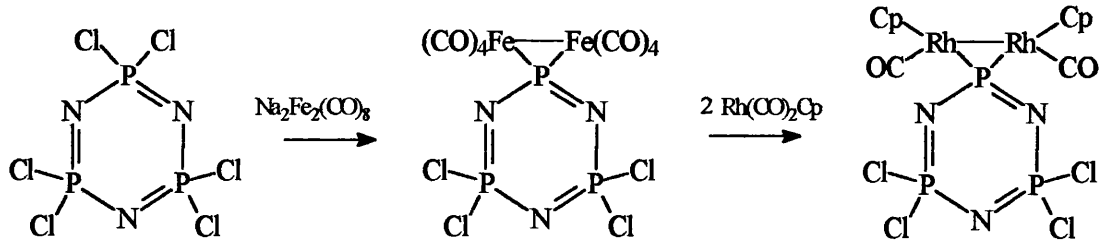
These type of compounds were discovered recently by Allcock and his co-workers[75] and the vast majority of the developments in this area have been at the cyclic trimer and tetramer level. $K^+[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ and the ruthenium equivalent react with $(NPF_2)_3$ to give simple, monosubstituted products (XII), (XIII), but, if the reaction is continued it is found that, unlike the iron complex, the ruthenium complex cannot form the uncyclised dimetallo complex (XIV), instead it goes straight through to the spirocyclic compound (XV). Scheme 1.6.7.

Scheme 1.6.7.


K[Fe(CO)2Cp]
K[Ru(CO)2Cp]
Cp(CO)2Fe
Ru(CO)2Cp
(XII)
(XIII)
K[Fe(CO2Cp]
K[Ru(CO)2Cp]
Cp(CO)2Fe
Fe(CO)2Cp
(XIV)
(XV)
hν

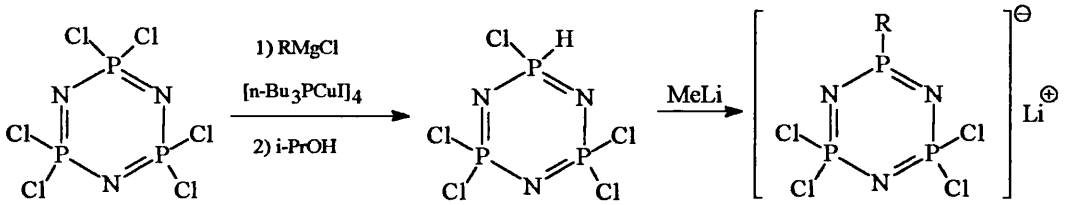
An alternative method of preparation is by metal - metal exchange.

Scheme 1.6.8.



A third method is to react phosphazene anions with organometallic electrophiles. Phosphazene anions are generally obtained from hydridophosphazenes (XVI) which in turn are made from organocopper reagents.[78]

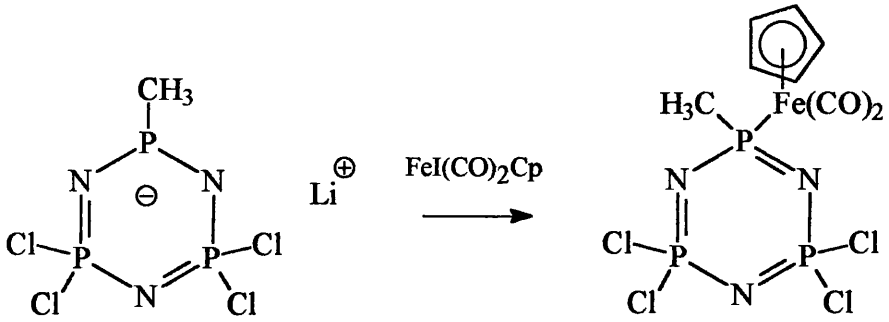
Scheme 1.6.9.



(XVI)

This phosphazene anion can now be reacted with organic electrophiles or with halogeno - transition metal carbonyl compounds.[79] Scheme 1.6.10.

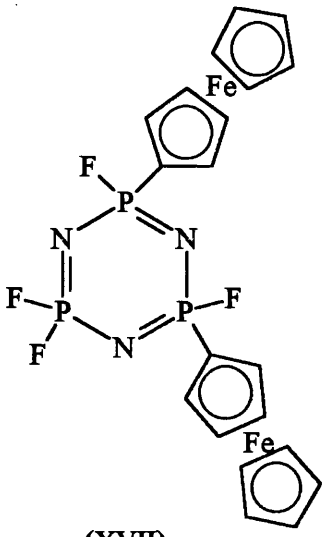
Scheme 1.6.10.



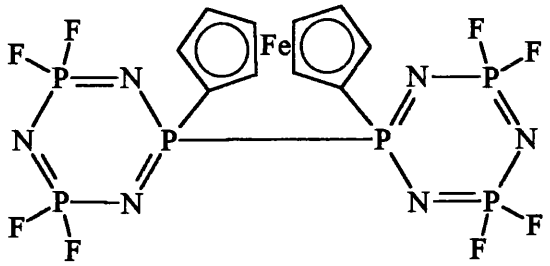
- iv) Transition metals can be linked to pendant spacer groups.

Making use of well established transition metal coordination reactions by interacting a metal with phosphazene side groups which possess terminal binding sites has resulted

such things as metallocene linked phosphazenes (XVII)[80] and (XVIII),[81] and the binding of iron porphyrins to phosphazenes.[82]



(XVII)



(XVIII)

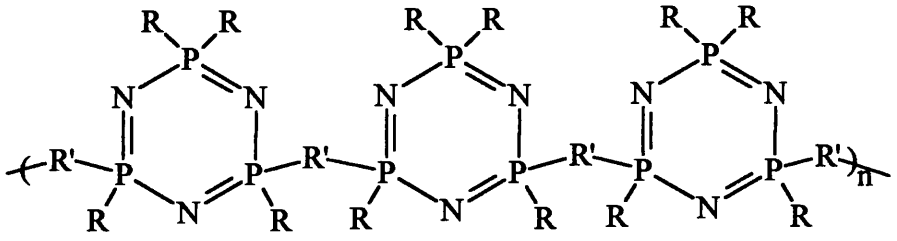
Connected with the metallocene complexes, it is also possible that complexes can be made that utilise the π-electrons of the phosphazene ring in the same manner.[83]

1.7 POLYPHOSPHAZENES

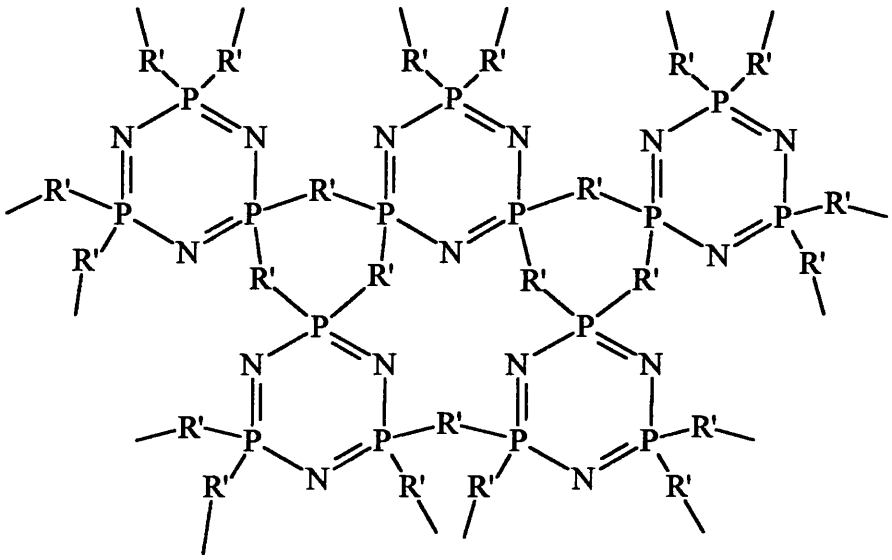
Polyphosphazenes comprise a broad class of inorganic macromolecules with the general formula $(NPR_2)_n$. They include one of the oldest known synthetic polymers and many of the newest, their structural versatility is vast and their uses and applications are as broad as in many areas of organic chemistry.

1.7.1 TYPES OF PHOSPHAZENE POLYMERS

Three types of phosphazene polymer are known: linear type macromolecules (III), cyclolinear polymers (XIX) and cyclomatrix resins (XX). These are shown in the diagram below



(XIX)



(XX)

1.7.2 HISTORY OF THE POLYPHOSPHAZENES

One of the first inorganic materials to be recognised as a linear macromolecule was the rubbery poly(dichlorophosphazene), "inorganic rubber", first synthesised in the late 1800's.[10, 37, 84] This was, however, found to be very difficult to handle at the time as it was completely insoluble and hydrolytically unstable in the atmosphere, and as a result only sporadic interest was shown in this system.

The eventual acceptance of Staudinger's[85] theory of long - chain macromolecules and the work of Meyer and Mark[86] in the 1920's and 1930's, which showed that natural rubber was a linear macromolecule, resulted in a slight resurgence of interest in this "inorganic rubber".

Work by Meyer, Lotmar and Pankow[87] strongly suggested that this material contained linear high polymeric chains, however, the general insolubility of the polymer, along with its atmospheric instability, discouraged serious interest. This situation persisted until the mid 1960's when it was realised[88] that the hydrolytic instability of poly(dichlorophosphazene) was due to the high reactivity of the P-Cl bonds and that this characteristic might actually be useful.

Allcock, Kugel and Valan[14] found that careful control of time, temperature and reactant purities yielded an essentially linear polymer that dissolved completely in organic solvents and that this could then react as a macromolecular reactant. Treatment with organic nucleophiles brought about total replacement of the chlorine atoms[89] to give hydrolytically stable poly(organophosphazenes), many of which possessed unusual and often useful properties.

With this discovery, interest in polyphosphazenes surged and since the mid 1960's literally hundreds of different poly(organophosphazenes) with a wide variety of side groups have been reported. Typically these polymers will have from 5,000 to 15,000 repeat units and can have molecular weights up to ~ 4,000,000.

1.8 LINEAR POLYPHOSPHAZENES

The linear polyphosphazenes are by far the most extensively studied of all the types of phosphazene polymer with virtually all of the applications thus far emerging from this class of material. In common with organic macromolecules, linear polyphosphazenes can also be branched or crosslinked as outlined in Section 1.0.

1.8.1 SYNTHESIS OF LINEAR POLYPHOSPHAZENES

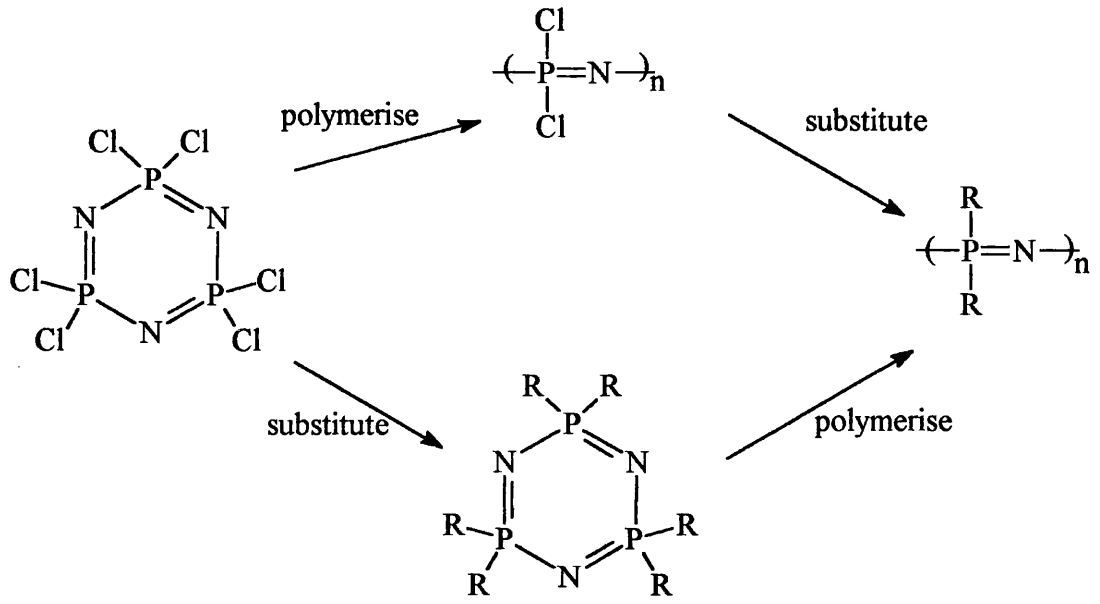
There are two major routes for obtaining linear polyphosphazenes: ring opening polymerisation and condensation polymerisation.

Ring Opening Polymerisation

By far the most extensively developed route to polyphosphazenes, ring opening of cyclic phosphazenes, can proceed in two ways, scheme 1.8.1.

The macromolecular substitution route involving polymerisation of hexachlorocyclotriphosphazene followed by substitution of the chlorine atoms with any of a variety of groups is the most commonly used method, both on a laboratory and commercial scale.

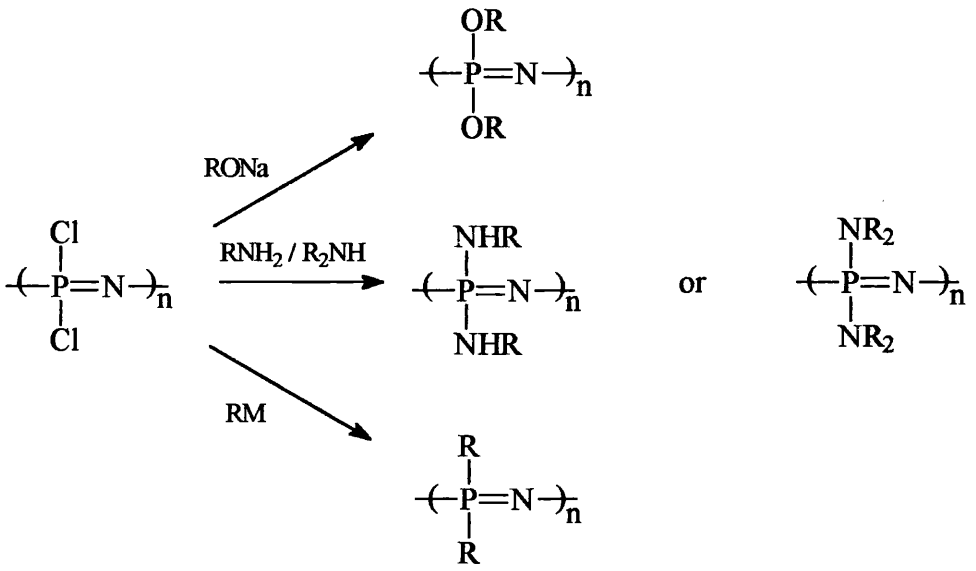
Scheme 1.8.1.



Hexachlorocyclotriphosphazene polymerises to the linear high polymer when heated in an evacuated, sealed tube for 24 to 48 hr. at 250 °C. When uncrosslinked, the polymer is a colourless, transparent, rubbery material which is soluble in organic solvents such as benzene, THF and toluene. It is stable in a dry atmosphere indefinitely, but, in a moist atmosphere, hydrolyses slowly to give phosphate, ammonia and hydrochloric acid. When in solution, poly(dichlorophosphazene) reacts rapidly and completely with nucleophiles, such as sodium trifluoroethoxide, to yield derivative polymers. The precipitation of sodium chloride is an impetus which helps drive the reaction to completion.

This route provides access to a vast number of differently substituted poly(organophosphazenes), with each their own set of physical and chemical properties which are dependent upon which side groups are present (Scheme 1.8.2). One of the few limitations to this proccess is the ability of certain bulky organic side groups to slow the replacement of nearby chlorine atoms by steric hindrance, resulting in the need for forcing conditions (high temperatures and long reaction times) in order to introduce such things as multi-rings or ortho-substituted aryloxy units. A method has been developed which aids the introduction of bulky substituents[90] in which tetrabutylammonium bromide is used as a phase transfer catalyst. However, as yet, this method has only really been applied to short chain and cyclic phosphazenes.

Scheme 1.8.2.



Inherent in the macromolecular substitution route is the possibility that two (or more) different side groups may be introduced. This can be done either simultaneously or sequentially.

A certain amount of control can be gained over this proccess by the use of bulky side groups, utilising the steric hindrance effects which slow the reaction rate after large amounts of chlorine atoms have been replaced. The remaining chlorine atoms can then be replaced by a less hindered nucleophile. For example, the treatment of poly(dichlorophosphazene) with diethyl amine results in the replacement of only one chlorine per phosphorus atom.[91] The other has been replaced by such things as methylamine, short chain alkoxides and alkyl/aryl organometallic reagents.

Polymerisation of organosubstituted cyclic phosphazenes is a method which has developed because of the difficulty of obtaining polymers with organic side groups, bound by a phosphorus - carbon bond, by the macromolecular substitution route. For example, reactions of $(NPCl_2)_n$ with such things as Grignard or organolithium reagents usually follow two concurrent pathways; substitution of chlorine by an organic group and cleavage of the phosphorus - nitrogen bonds in the skeleton.[92] This cleavage of the skeleton occurs by coordination of the organometallic reagent to nitrogen atoms in the backbone of the polymer. Any structural feature of the polymer which encourages this, such as the introduction of alkyl or aryl organic groups, also encourages chain cleavage.

One technique which has been utilised to try to overcome this problem is to substitute most of the halogen atoms in a poly(dihalogenophosphazene) with an electron withdrawing organic group, (e.g. trifluoroethoxy), thus stabilising the

backbone, followed by the introduction of alkyl, aryl or carboranyl groups.[93] An alternative to this is the polymerisation of cyclic phosphazenes which already contain organic substituents.[94]

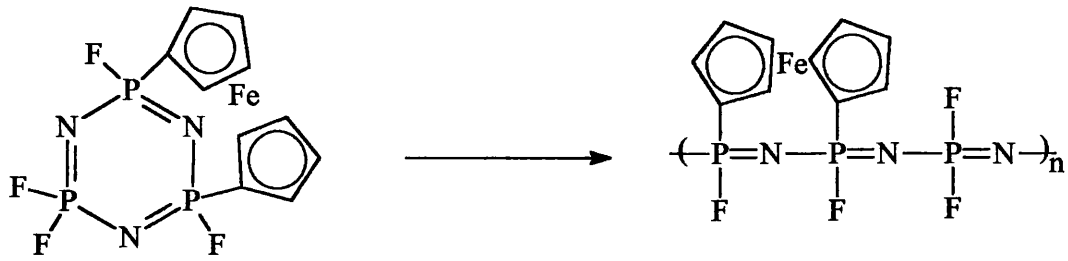
It is much easier to substitute cylic trimeric phosphazenes with organic groups by the use of organometallic reagents and the consequences of skeletal cleavage are much less severe, however, problems are encountered when polymerisation is attempted. Cyclic phosphazenes with one or two organic groups can be polymerised,[95] e.g. $N_3P_3Cl_5R$ (R = Me or Ph) and $N_3P_3Cl_4(CH_2SiMe_3)R$ (R = alkyl or phenyl), often as easily as $(NPCl_2)_3$ itself, however, there is a tendency for polymerisation to decline as more and more organic groups are added.[96]

To date there is only one fully substituted cyclic phosphazene known which will undergo ring opening polymerisation, $N_3P_3(OCH_2CF_3)_4[(C_5H_4)_2Fe]$ and this requires the presence of a catalytic amount of $N_3P_3Cl_6$.[97,98]

Other fully substituted species are known to undergo ring expansion to higher homologues, for example, when heated, $(NP(Me)_2)_3$ undergoes ring - ring equilibration to the cyclic tetramer.[99]

If the phosphazene ring is subjected to strain then this facilitates polymerisation. Transannular bridged phosphazenes, for example, can open to give metallocene bridged polymers[98] and some spirocyclic species undergo ring opening polymerisation.

Scheme 1.8.3



1.8.2 MECHANISM OF RING OPENING POLYMERISATION

Experimental facts which have been reported include:

- i) Uncatalysed $(NPCl_2)_3$ polymerisation is very slow below 210°C but increases rapidly with temperature in the 220 - 230°C range.[14, 100]
- ii) Phosphazene tetramers polymerise more slowly than the corresponding trimers.[100]

- iii) Along the series $(NPBr_2)_3$, $(NPCl_2)_3$ and $(NPF_2)_3$ progressively higher temperatures are needed to effect polymerisation.[101]
- iv) The polymer formed from the bulk polymerisation of $(NPCl_2)_3$ undergoes cross-linking when 75% of the trimer has been consumed.[14]
- v) Poly(dichlorophosphazene), when free from oligomers, slowly cross-links in benzene at 25°C[14]
- vi) High pressure experiments suggest that the transition state for the rate determining step has a larger volume than the reactants in that step.[102]
- vii) The polymerisation is catalysed by such species as carboxylic acids and their salts, ethers, ketones, alcohols and some metals (e.g. zinc, sodium and tin).[103]
- viii) Free radical catalysts such as benzoyl peroxide and azobis(isobutyronitrile) appear to have little effect on the polymerisation.[100] UV irradiation has no accelerating effect on the polymerisation.
- ix) ESR experiments with purified, molten $(NPCl_2)_3$ at 250°C suggest the absence of free radical species.[104]
- x) Below the polymerisation temperature range, molten $(NPCl_2)_3$ has a low conductivity and a low dielectric constant, above these temperatures they both rise rapidly with temperature and continue to rise even when the temperature is held steady.

Very different observations have been made for $[NP(OPh)_2]_3$.[103] These experimental observations have been interpreted in terms of an ionic, chain propagation process.[105]

Initiation:

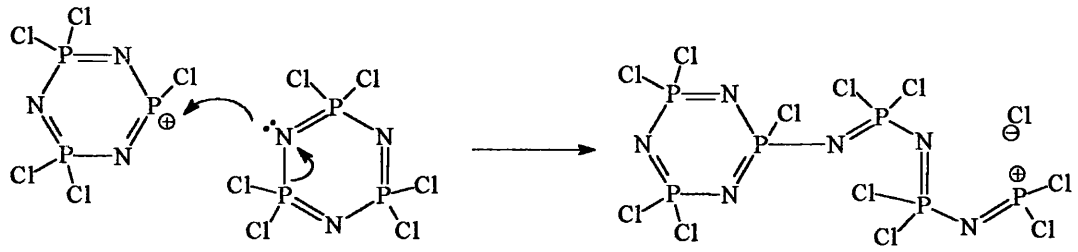
The heating of the halogenophosphazene induces ionisation of a phosphorus - halogen bond. This is consistent with the conductivity and capacitance measurements, with the role of catalysts in the polymerisation (i.e. all of the catalysts have the ability to facilitate removal of halogen from P-X) and with the observation of polymerisation temperatures in the halogen series.

Other possible initiation processes can be discounted due to the experimental observations, for example, homolytic cleavage of a P-N bond in the phosphazene ring is eliminated because no evidence of free radical participation in the polymerisation has been found. The more likely, heterolytic cleavage of the skeleton, is also ruled out from the observations of the conductivity and capacitance behaviour of $[NP(OPh)_2]_3$ which imply that this does not occur.

Propagation:

It can be envisaged that this cyclic cation could now attack a further phosphazene ring and result in a chain propagation process.

Scheme 1.8.4



The presence of a growing, linear cation - anion complex would be consistent with the observed dielectric constant data and also with the high pressure reaction data. The lower rate of polymerisation of the tetramer could be explained by the greater shielding of a ring nitrogen atom to electrophilic attack by the puckered conformation of the tetrameric ring over the planar conformation of the trimeric ring.

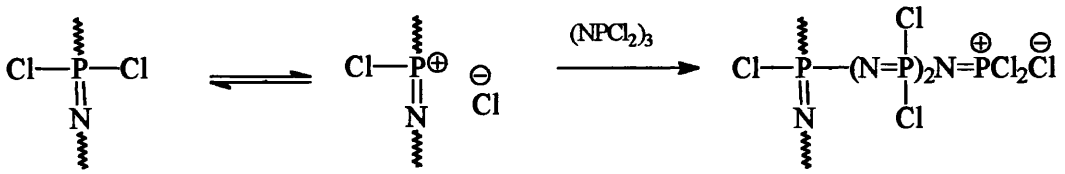
Termination:

It can be seen that the polymerisation would be slowed greatly by lowering the temperature as this would result in a reduced degree of dissociation of the P^+ Cl^- ion pair. As there would be a residual degree of ionisation remaining it can also be seen why slow cross-linking is observed at 25°C.

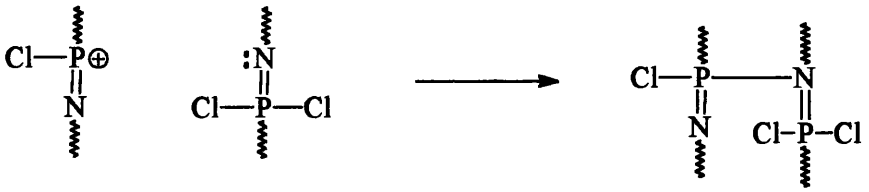
Branching:

Branching, and indeed cross-linking, could arise if ionisation of a chlorine from a middle chain unit occured.

Scheme 1.8.5



and



There are shortcomings with this mechanism, the most obvious being that it doesn't explain why some fully substituted cyclic phosphazenes undergo ring expansion since obviously these materials do not have a phosphorus - halogen bond which can be ionised and, as yet, no data is available which helps explain these observations.

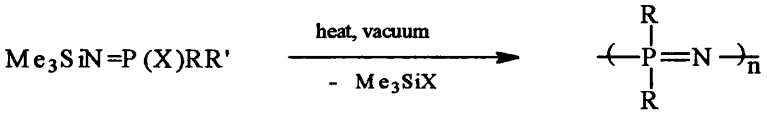
This is also by no means the only mechanism which has been proposed, others include cationic,[106] anionic[107] and even free radical mechanisms,[108] but, consideration of the vast majority of the available experimental data supports the described mechanism rather than any of the others.

1.8.3 CONDENSATION POLYMERISATION

It can be envisaged that, in common with the various condensation syntheses of cyclic phosphazenes, polyphosphazenes should be accessible via a natural extension of such reactions.

It is known that condensation of $Cl_3PNP(O)Cl_2$ yields poly(dichlorophosphazene),[109] however, this material is unstable in the atmosphere and needs to be stabilised by replacement of the chlorine atoms in ways which have been discussed already.

A reaction which was developed by Neilson and Wisian-Neilson[110,111] for the formation of poly(organophosphazenes) involves the thermal decomposition of N-silyl phosphoranimines.



(9)

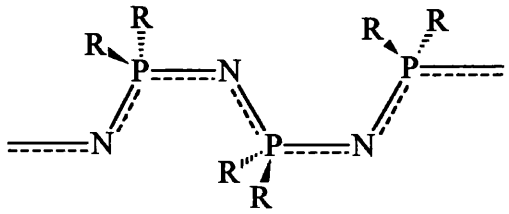
For reasons which are not fully understood, X needs to be OCH_2CF_3 for polymer formation, other leaving groups, such as Br, yielding only cyclic phosphazenes.

Unlike the macromolecular substitution route this route provides relatively easy access to poly(phosphazenes) which contain P-C bonds to side groups, however, as yet only a limited number of side groups can be incorporated into the polymer, these include Me, Ph, CH_2E (where E = R_2P or $SiMe_2R$)[112] and their combinations. Polymers obtained by this method generally have low to medium molar masses (~50,000) with fairly narrow polydispersities (~ 2 typically) and studies have revealed fairly high molar masses early in the reaction thus indicating a chain growth mechanism.[111]

Work by Matyjaszewski has shown that the polymerisation may be assisted by the presence of initiators. The polymerisation of $Me_3SiNP(OCH_2CF_3)_3$ in the presence of anionic initiators, such as Bu_4NBr, is possible at temperatures and times far below those required for ring opening polymerisation, for example.[113]

1.8.4 PROPERTIES OF LINEAR POLYPHOSPHAZENES

Polyphosphazenes contain one of the most flexible skeletons known in polymer science, the dπ-pπ type bonding in phosphazenes, mentioned previously, means that the inherent torsional barrier in the chain is much smaller than in organic polymers, this barrier may be as low as 418 J per bond.[114] The reason for this is that each phosphorus atom can use as many as five 3d orbitals, meaning that movement of a P-N bond can bring the nitrogen $2p_z$ orbital into an overlapping position with a d-orbital, at virtually any torsional angle. Because of this great skeletal flexibility the conformation adopted by a polyphosphazene chain can be understood in terms of the attractions or repulsions of side groups on that chain. The situation with polyphosphazenes is much simplified over the equivalent of organic polymers as the side groups are located on every other backbone atom, with the result that a cis - trans planar type conformation would be that with the lowest energy (XXI).



(XXI)

X-ray studies have confirmed that this conformation, or a slightly distorted version, is indeed that adopted by most polyphosphazenes[16,114,115] studied to date, however, data from polymers with complex side groups is difficult to assess and much more work is required in this area.

The nature of the side groups in polyphosphazenes can alter the overall properties of the polymer, indeed, it is this which makes possible the vast potential for such varied applications as are observed in phosphazene chemistry. For example, the hydrophilic or hydrophobic nature of a poly(phosphazene) is determined by the degree to which the side groups can shield the hydrophilic backbone, and on the nature of the side groups themselves. e.g. methyl groups are small enough not to shield backbone nitrogen atoms (the source of the skeletal hydrophilicity) and thus methylphosphazene polymers are hydrophilic. Groups such as trifluoroethoxy or phenoxy, however, are large enough to shield the skeleton (and are hydrophobic themselves) and so the resulting polymers are strongly water repellant and are soluble in organic solvents.

If hydrophilic side groups are present, such as glyceryl or $NHCH_3$ then the polymer can be water soluble.[117] If suitable side groups are chosen, polymers which are unstable in water and which have non-toxic hydrolysis products, can be synthesised. These polymers have important biomedical applications.

The glass transition temperature of polyphosphazenes is greatly affected by the particular side group on the polymer (Table 1.8.1). If large, inflexible groups are present the inherent flexibility of the backbone can be affected by steric interferences. If small, or very flexible side groups are present some of the lowest Tg's known in polymer chemistry are observed.

Table 1.8.1 Some representative Tg's of polyphosphazenes.

Material	Tg (^{o}C)	reference
$[NP(OPh)_2]_n$	-8	14
$[NP(OC_6H_4C_6H_5\text{-}p)_2]_n$	+93	36
$[NP(OCH_2CH_2CH_2CH_3)_2]_n$	-105	116
$[NP(OCH_2CH_2CH_3)_2]_n$	-100	116
$[NP(NHC_6H_5)_2]_n$	+91	14,91

When small rigid side groups are present, and when these are the only type of side group, then microcrystalline domains can be observed in poly(phosphazenes). These have the effect of stiffening a material and raising the temperature at which it may be used. Polyphosphazenes with side groups such as F, Cl, OCH_2CF_3 and some substituted phenoxy groups have displayed microcrystallinity.[14,118]

Polyphosphazenes with side groups which can interact with each other, e.g. stack or "inter-leaf" with those from another polymer, can display unusual optical and electrical properties.[119] Liquid crystalline properties can be displayed by some polyphosphazenes which have appropriate side groups such as biphenyl units.[120]

1.8.5 DEPOLYMERISATION

In common with other heteroatom polymer systems, such as poly(organosiloxanes) and poly(oxymethylenes),[121] polyphosphazenes undergo depolymerisation. When heated to elevated temperatures poly(organophosphazenes) as well as poly(dihalophosphazenes) depolymerise to yield a series of cyclic phosphazenes. This process is not the same as decomposition, although, in some cases decomposition does occur before depolymerisation. A knowledge of what affects depolymerisation is important as this affects the usable temperature range of a polyphosphazene and hence its possible applications.

The exact temperature at which depolymerisation begins depends upon the nature of the side groups in the polymer, for example, poly(organophosphazenes) tend to depolymerise at lower temperatures than poly(dihalophosphazenes), however, all systems share the fact that polymerisation and depolymerisation is really an equilibrium process rather than two separate events. This has been shown by the fact that if separate samples of chlorophosphazenes are heated in sealed systems, no matter what the starting composition, (of trimer, tetramer and polymer for example) the same final composition is observed.[122]

If a mixture, while being heated, had the amount of trimer or tetramer increased then the amount of polymer in the system was also observed to increase. If the temperature was increased then the amount of observed polymer decreased. These observations, suggesting an equilibrium in which the polymerisation step is exothermic, have been made by several workers.[122, 123]

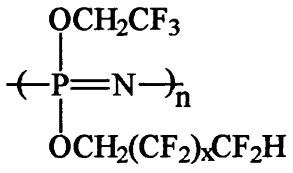
Depolymerisation has also been observed by Thermogravimetric and Differential Thermal Analysis as weight loss has been observed as polymer samples were heated.[124]

The mechanism of depolymerisation is still unclear and several ideas have been put forward. These are discussed in Section 5.2.

1.8.6 APPLICATIONS OF LINEAR POLYPHOSPHAZENES

Because of the ability to tailor the properties of a poly(phosphazene) by changing the side groups on it, there are a vast array of different applications open to these materials. These range from automotive devices to sensitive, controlled drug release systems of which the following are but a few examples.

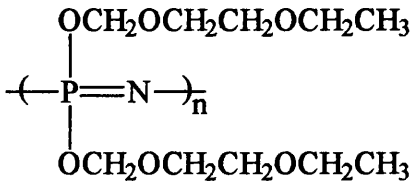
The first poly(phosphazenes) to be developed commercially had two different types of fluoroalkoxy side groups on the same backbone (XXII).[36, 125]



(XXII)

The two side groups are added simultaneously and compete for replacement of the chlorine atoms with the result that a random distribution of the side groups is probably obtained. These materials are generally cross-linked during fabrication and fillers such as carbon black are added to reduce deformation of the final product. As a result of the observed resistance to hydrocarbons and of the flame resistance[5] these materials are used for such things as fuel lines, O-rings and gaskets in the aerospace industry.

Poly[bis(methoxyethoxyethoxy)phosphazene], MEEP (XXIII), has found use in battery technology.[126]



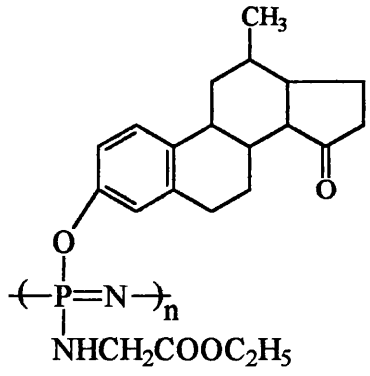
(XXIII)

Flexible polymers which contain ether side groups (or backbone units) can function as solid solvents for salts such as lithium triflate ($LiSO_3CF_3$) and these systems can act as ionic conductors of electricity. This occurs by ion pair separation followed by transferral of the cation from one chain to another provided that the side groups are flexible enough. If an electric current is applied then these cations will migrate to the cathode and the anions to the positive electrode.

The application of this principle is in the fabrication of lightweight, high energy density, rechargeable lithium batteries. Until recently the polymer of choice was poly(ethylene oxide), however, this material is microcrystalline and so ionic conduction can be interrupted in these domains. High conductivity can only be obtained at 100°C. MEEP on the other hand is non-crystalline and has an ionic conductivity 1000 times greater than poly(ethylene oxide) at room temperature.

Water soluble, bioactive polyphosphazenes have been developed which are capable of being drug delivery systems. For example, the platinum complex, cis-$(NH_3)_2PtCl_2$, is a known anti-tumour agent, however, this complex is water soluble and is readily excreted through the kidneys cuasing severe damage. Poly[bis(methylamino)phosphazene], $[NP(NHMe)_2]_n$, has been used to replace the ammonia ligands in the complex (where coordination involves the backbone nitrogen atoms in the polyphosphazene) as it is non-excreteable while still being water soluble.[70]

Bio-erodable polyphosphazenes are also used as drug delivery systems in which, this time, the polymer breaks down to non-toxic materials. An example is the controlled release of steroids by polyphosphazenes which contain ethyl glycinate groups (XXIV).[127]



(XXIV)

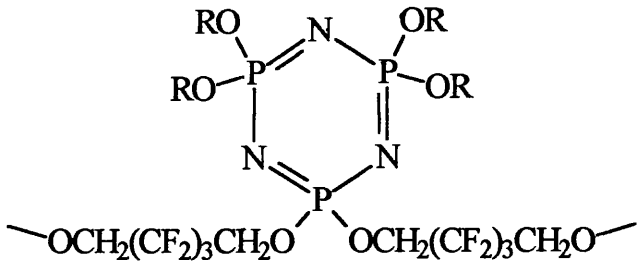
1.9 OTHER TYPES OF PHOSPHAZENE POLYMERS

Although linear macromolecules are by far the most studied and most common of the polyphosphazenes, they are not the only type. Materials ranging from inorganic ceramics to organic copolymer systems with cyclophosphazene side groups are known.

1.9.1 CYCLOLINEAR POLYMERS

The development of these materials resulted from attempts to combine the high thermal stability of the phosphazene ring with the flexibility and elastic properties of a polymer. Indeed, polymers of this type are known which are elastomeric, stable in air up to a temperature of 250°C and which are resistant to aqueous media as well as to common organic solvents. One possible general structure for these materials is shown, (XIX), ($R = CH_2CF_3$).[128]

An example of this type of material is (XXV)



(XXV)

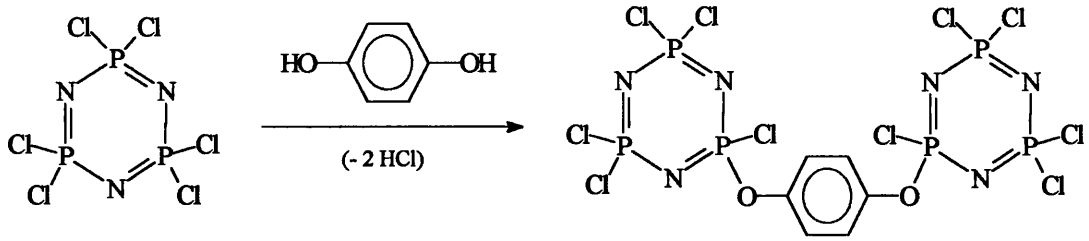
This material is made by initially reacting hexachlorocyclotriphosphazene with ammonia to yield a diamino derivative. This is followed by replacement of the remaining chlorine atoms by reaction with the sodium salt of trifluoroethanol. Final reaction with fluorinated poly(methylene α,ω-glycols) yields the cyclolinear polymers.

1.9.2 CYCLOMATRIX POLYMERS

If all of the halogen atoms in a halocyclophosphazene are available for reaction with a difunctional reagent then a highly cross-linked ultra-structure can be formed. These materials are known as cyclomatrix polymers and have the general structure depicted in (XX). Cyclomatrix materials have been described as either rubbery solids or tough resins, they are stable with continuous use at 250°C and even for occasional use at 500°C, they are highly resistant to acids, alkalis and organic liquids and they have a high impact strength.

Some cyclomatrix polymers have been made on a commercial scale,[129] either in the melt or in solution. For example:

Scheme 1.9.1.



Replacement of additional chlorine atoms results in enhanced cross-linking.

When carried out in solution, soluble pre-polymers are generally obtained which are much easier to handle in terms of processing of the materials. Crosslinking can be completed by treatment of these pre-polymers with such things as formaldehyde.

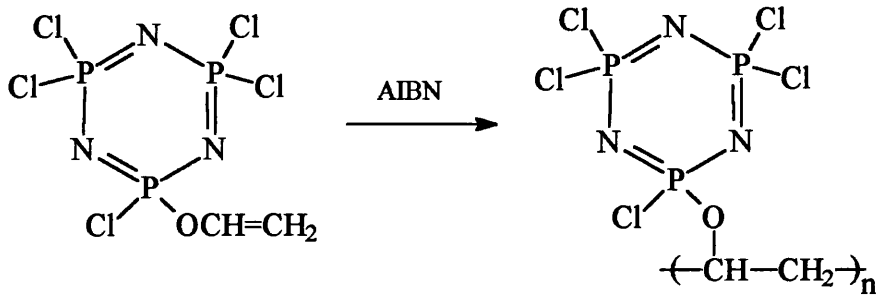
Possible uses for cyclomatrix polymers include heat resistant electrical components and wire coatings, structural adhesives for high temperature applications and even as radiation resistant components in nuclear reactors.

1.9.3 ORGANIC POLYMERS WITH CYCLOPHOSPHAZENE SIDE GROUPS

By chemically binding a phosphazene to an organic polymer, flame retardency can be introduced into the material. (Previously, a flame resistant Rayon was manufactured which consisted of alkoxyphosphazenes physically dispersed in the organic polymer fibres.[131])

A typical method for producing these materials is to polymerise a vinyl side group on a cyclic phosphazene.[132]

Scheme 1.9.2.



Copolymerisation of these vinyl substituted phosphazenes is also possible with such species as styrene.

1.10 INTRODUCTION TO ULTRASOUND

All chemists will be aware of the various methods available to them to introduce energy into a chemical system in order to bring about some change. These methods include the use of heat, high pressures, radiation and agitation. One method, however, which is probably more unfamiliar to a great many workers is the use of high power ultrasound.

Ultrasound will be familiar to a great many people through its more widely known applications such as in navigation systems (SONAR), in nature (bat navigation) and in medical diagnosis (scanning), however, the limit of most chemists' knowledge of the application of ultrasound in the laboratory probably only stretches to use as a method for increasing the efficiency of dissolving a material and as an effective method for cleaning glassware.

1.10.1 WHAT IS ULTRASOUND?

In its broadest sense, ultrasound can be defined as any sound which is of a frequency above that to which the human ear can respond. This lower limit is generally taken to be 20kHz (the typical range for human hearing is approximately 6Hz. to ~18Hz., however, this can vary widely between different people) and there is effectively no upper limit, but generation of frequencies greater than around 5MHz is at the present time very difficult.

As can be imagined, over such a wide range of frequencies a great many effects can be observed, but, there are effectively two types of ultrasound which are utilised.

a) low amplitude - high frequency (2 - 10MHz.) and,
b) high amplitude - low frequency (20 - 100kHz.)

The first of these is known as *diagnostic ultrasound* and its applications concern the effect of the medium on the wave. The second is *power ultrasound* and applications in this case concern the effect of the wave on the medium. It is power ultrasound which is utilised in "sonochemistry", the use of ultrasound as a source of energy in a chemical reaction.

1.10.2 GENERATION OF ULTRASOUND

The generation of sound with such high frequencies relies on the Piezoelectric effect, first established in 1880 by Curie.[134] In some materials e.g. quartz, the application of a potential difference across the faces of a crystal of that material will result in dimensional changes in that crystal. The use of an alternating current results

in the conversion of electrical energy into vibrational energy. By varying the piezoelectric material used various powers and frequencies can be generated.

There are various ways of transferring this generated ultrasound to a reaction mixture, the two most common of which are by the use of an ultrasonic cleaning bath or a direct immersion ultrasonic horn/probe. An ultrasonic cleaning bath consists of a well of water underneath which is either one or many ultrasonic transducers. The efficiency and overall power transferred to a reaction vessel, which is immersed in the water, depends on the size of the bath and on the positioning of the vessel inside it. Temperature control is difficult when using an ultrasonic bath for sonochemical purposes.

An ultrasonic horn, or probe, is immersed directly into the reaction mixture and transfers the ultrasound in much the same way as a tuning fork works, that is, the tip of the probe vibrates. Greater powers can generally be obtained with a probe as they have less energy losses than a bath. Also, probes have the facility that they can be tuned to give optimum effects, however, erosion of the probe tip can occur with prolonged use resulting in contamination of a reaction mixture with metallic particles.

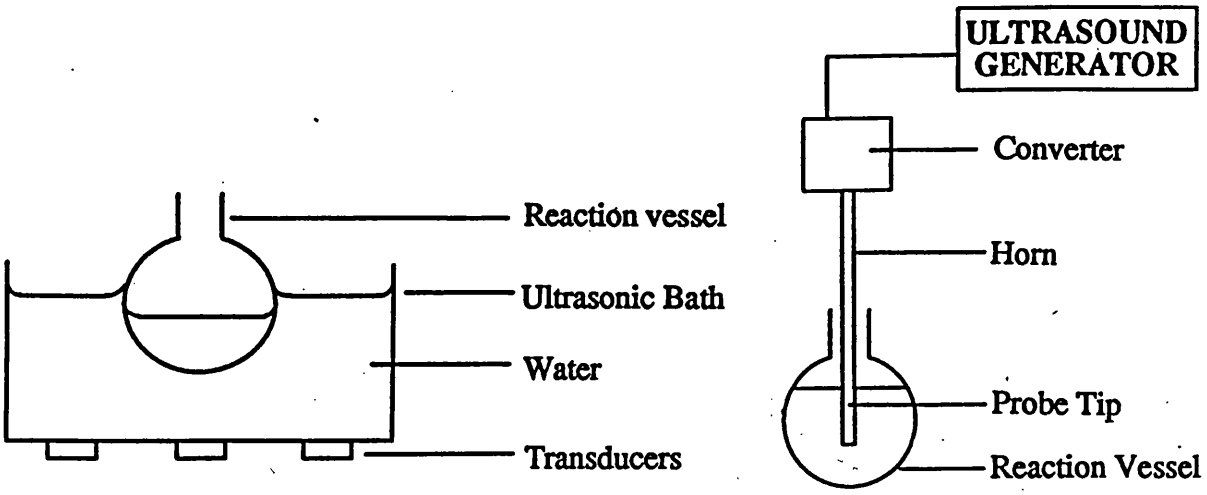


Figure 1.10.1. Ultrasonic bath and probe systems.

1.10.3 THE EFFECT OF HIGH INTENSITY ULTRASOUND ON LIQUIDS

Sound is transmitted as a longitudinal wave consisting of compressions and rarefactions and it could be envisaged that, as in photochemistry, these waves may interact directly with any chemical bonds present. However, it can be shown that for a typical sonochemical reaction (20 - 50kHz.) the wavelengths produced are in the order of 3 to 7cm. (since c, the speed of sound in liquids, is ~1500ms^{-1}). Clearly, no direct

coupling to chemical bonds can be occuring and observed sonochemical effects are due to an indirect effect known as *cavitation*.[135]

If the ultrasonic generator is considered to be like a piston, then the forward stroke creates pressure which is transferred through the liquid by a series of molecular interactions. When this effect is combined with that of the backward stroke the net result is that molecules tend to oscillate about their mean positions.

If the negative pressure generated is sufficiently high then it can overcome the intermolecular cohesive forces in the liquid causing the molecules to be torn apart from each other, with the result that tiny cavities or microbubbles are formed in the liquid. This is especially so if dissolved gas or suspended solid particles can act as nucleation sites. Solvent vapour and/or dissolved gases can then enter the bubble preventing it's total collapse on the next compression. This process is repeated with following cycles until the bubble grows to a size of 100 - 200 μm where it comes into resonance with the acoustic field and eventually undergoes a rapid expansion and violent collapse. This is shown schematically in Figure 1.10.2. The energy utilised in sonochemistry arises from this process.

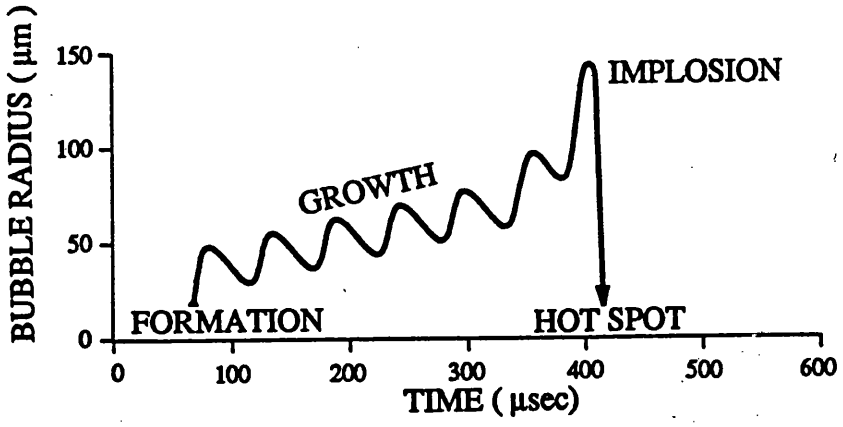


Figure 1.10.2 Schematic representation of the cavitation process.

This phenomenon is known as cavitation and consists of three discrete stages

a) nucleation
b) bubble growth
c) implosive collapse

and the dynamics of growth and collapse depend upon the local environment

Some theoretical calculations performed by Noltingk and Neppiras[136] predict values of 1000 - 2000 bar for the pressure and 4000 - 6000K for the temperature upon

collapse. This has been backed up by some sonoluminescence work performed by Suslick and co-workers[137] in which short flashes of light were observed during cavitation. The luminescence spectra for sonicated alkanes were observed to be very similar to those from species involved in combustion at temperatures of several thousand Kelvin.

Depending on the conditions, two types of cavitation may be observed in sonochemical systems, transient, and stable. Transient cavitation bubbles have short lifetimes of one or two acoustic cycles and they consist of voids or vapour filled bubbles. Collapse of transient cavitation bubbles is very violent. Stable cavitation bubbles have longer lifetimes, generally of the order of many acoustic cycles and consist mainly of gas filled bubbles. The collapse of stable cavitation bubbles is less violent than that of transient cavitation bubbles, however, oscillation of the bubbles causes great disruption and movement of adjacent molecules.[133,138]

1.10.4 FACTORS INFLUENCING CAVITATION

The nature of the ultrasound

The ultrasonic frequency is very important as it determines the amount of time a cavitation bubble has to grow.[142] It has been found that an increase in frequency leads to a decrease in the amount of cavitation.[143]

The ultrasonic intensity, I, is defined as the energy transmitted through unit area of the medium in unit time and is given by

$$I = \frac{P^2{}_{max}}{2\rho c} \qquad \text{i.e. } I \propto P^2_{max}$$

where c is the velocity of sound in the medium, ρ the density of the medium and P_{max} the pressure generated within the bubble at the moment of collapse. P_{max} has been estimated based upon the intensity of the sound used.

It has also been estimated[140] that;

$$T_{max} = T_o\left(\frac{P_{max}(\gamma-1)}{P}\right)$$

where T_{max} = temperature generated within the bubble at the moment of collapse

T_0 = ambient temperature

P = pressure in the bubble at its maximum size

γ = the ratio of the specific heats of the gas or vapour

and hence an increase in ultrasonic intensity will result in an increase in the temperatures and pressures produced on bubble collapse. The accuracy of these estimates were checked by comparing expected chemical effects to those actually observed. However, ultrasonic intensity cannot be increased indefinitely, at some point the bubble will grow so large that there is insufficient time for collapse.[136,144]

The solvent

Physical properties such as viscosity would be expected to affect the cavitation process as the formation of a cavity in a liquid requires the negative pressure of an acoustic cycle to overcome cohesive forces in that liquid. It has been shown that in more viscous fluids cavitation is more difficult, although this is a small effect.[139]

Of more importance to cavitation is the vapour pressure of the solvent,[140] high vapour pressures can result in the void created being occupied by some solvent vapour which can act as a cushion thus making collapse less violent[141] and lessening chemical effects.

Temperature

Increasing the temperature of the system results in an increase in the vapour pressure over the liquid and hence also increases the cushioning of collapse.

Applied pressure

The application of pressure to an ultrasonic system has mixed results. On the one hand, a decrease in solvent vapour pressure will result, with the effect of an increase in the effective power of cavitational collapse. On the other, bubbles beneath a certain size will be unable to grow, with the result that the amount of cavitation decreases.

Dissolved gases

Gases dissolved in the solvent reduce both the intensity of the cavitation and the cavitational threshold. This is due to the gas penetrating into the cavitation bubbles and cushioning collapse,[145] also the presence of dissolved gas increases the number of cavitation nuclei present in the system and hence lowers the cavitation threshold,[146] the value of the applied acoustic pressure necessary before cavitation occurs.

1.11 INFLUENCE OF ULTRASOUND ON CHEMICAL REACTIONS

Ultrasound has been applied to a great many reactions with a variety of effects being observed. For example, reactions may be accelerated or less forcing conditions

employed,[147] induction periods can be significantly reduced, the need for reaction initiators can be reduced or even eliminated[148] and it is even possible to change a reaction pathway with the result of ultrasound.[149]

These effects come about for a variety of reasons. i.e. if some different types of reaction are considered:

- i) Heterogeneous, solid - liquid systems

In this type of reaction it is possible to get cleaning of the solid surface by pitting[150] caused by high intensity shock waves from the collapse of a cavitation bubble hitting the solid surface and by microstreaming.[151] A jet of solvent is thrown from a collapsing cavitation bubble and hits the solid surface at high speed. The clearing away of reaction products from reaction sites by the same processes and a reduction in solid particle size due to fragmentation caused by cavitational collapse lead to an increase in reactive surface area.

Improved mechanical stirring, as a consequence of acoustic streaming from a probe tip for example, results in improved mass transport and the use of ultrasound to replace or aid phase transfer catalysis.

- ii) Heterogeneous, liquid - liquid systems.

Ultrasound can be used to form very fine emulsions (and indeed is in the food industry[152]) thus increasing surface contact of reactive species in a reaction and promoting mass transfer.

- iii) Homogeneous liquid systems.

The very high temperatures and pressures acting upon the vapour inside cavitation bubbles can result in the relatively easy formation of radicals.[153] This has the consequence that in some systems a change in reaction pathway (ionic to radical) may be observed.[149]

1.11.1 ULTRASONIC DEGRADATION OF POLYMERS

The application of ultrasound to polymers considerably predates its use in other chemical applications. For example, as early as 1933 it was observed by several workers[154] that, upon treatment with ultrasound, solutions of natural polymers such as starch, gum arabic, and gelatin experienced a reduction in viscosity. This viscosity reduction was attributed to a breakdown of the polymer molecules.

Bond breakage was firmly established by Brohult[155] who, using an ultracentrifugation technique, found that upon treatment with ultrasound, haemocyanin

fragmented into monodisperse fractions. This was further confirmed by Schmid and Rommel[156] who observed permanent viscosity decreases in solutions of polystyrene and polyacrylates when sonicated. These workers also noted that the decrease in viscosity was initially rapid, but, that it slowed with time and eventually reached a limiting value, M_{lim}. This has since been noted by a number of workers and is now generally regarded as a characteristic of ultrasonic degradation.[157]

1.11.2 EFFECT OF DEGRADATION ON MOLAR MASS DISTRIBUTION

Because of the small variety of analytical techniques which were available initially, few studies of changes in the molar mass distribution were carried out. The first, by Jellinek and White[158] used fractional precipitation of poly(styrene) samples and determined the molar mass of each fraction viscometrically. It was found[159] that when samples of initially narrow distribution were sonicated then the polydispersity first broadened and then narrowed again as M_{lim} was approached Shaw and Rodriguez[160] found that after long sonication times samples of poly(dimethylsiloxane), with initially different distributions, approached the same distribution. Similar results for other polymers have also been observed.[161]

The first suggestion that non-random degradation was occurring was put forward by Gooberman and Lamb[162,163] whose sonication of polystyrene samples revealed secondary peaks at lower molar mass in the distribution were appearing. This non-random degradation was again demonstrated[164] after the advent of GPC by Moore[2] allowed changes in the molar mass distribution to be measured more easily. Narrow distribution polystyrene was sonicated in THF and chromatograms showed secondary peaks at approximately half the molar mass of the original polymer. This was compared with degradation by benzoyl peroxide in which random cleavage was observed. This work also indicated that bond cleavage occurs at or near the centre of the macromolecular chains and this again is now generally considered to be a characteristic of ultrasonic degradation.

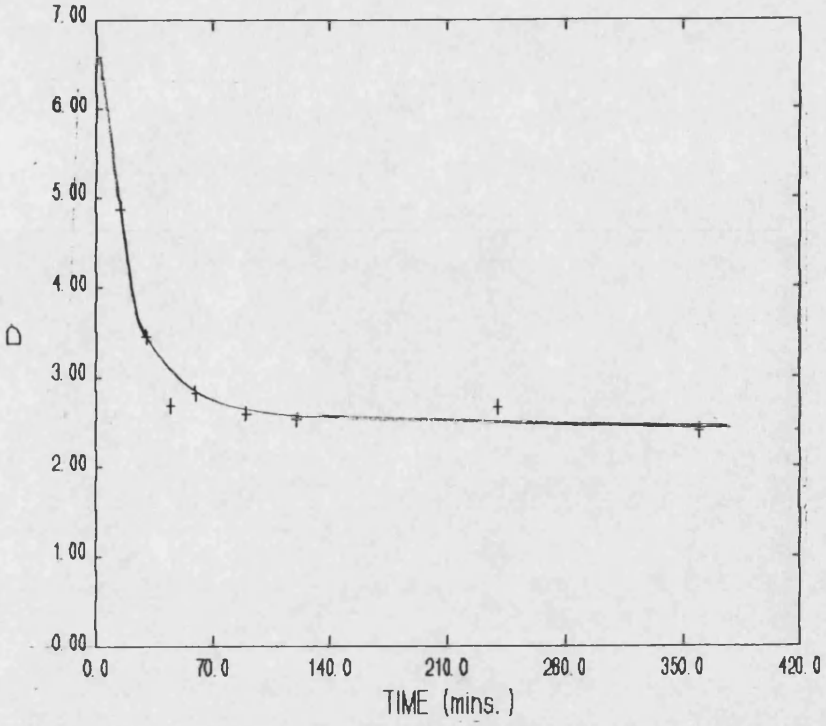


Figure 1.11.1. The effect of sonication on the molar mass distribution of a polymer sample.

1.11.3 INFLUENCING FACTORS ON DEGRADATION

The vast majority of work in this area has been carried out on organic polymers with only limited studies performed on inorganic materials, such as polysiloxanes and polyorganosilanes. As a result the following discussion concentrates predominantly on these organic studies, however, the trends noted can be applied to most inorganic systems also.

If, as was suspected, degradation was occuring as a result of cavitation then those influences on cavitation mentioned previously should also affect degradation.

The nature of the ultrasound

Mostafa[165] found degradation to be frequency dependent and observed a maximum rate of degradation at ~1MHz., beyond which degradation decreased. This frequency dependence has been observed by other workers.[166]

Higher intensities have been shown to result in faster degradation in a number of systems[167] and Jellinek[166] has shown the degradation rate constant to be a linear function of intensity. It is generally agreed that M_{lim} decreases with increasing intensity although some workers have described an optimum intensity[168] whereby the number of cavitation bubbles becomes so high near to the ultrasonic source that they disrupt the passage of sound deeper into the liquid and hence reduce the efficiency of the degradation.

The solvent

The solvent used in a degradation has been found to be important, as when polystyrene was sonicated as a suspension in water, no degradation was observed.[170] Similarly, when acetone (a non-solvent) was added to solutions of polystyrene in benzene the rate of degradation was found to decrease. This indicates the size and shape of a polymer in solution is important and attempts have been made to correlate degradation with the thermodynamic quality of the solvent. Golubev et al.[171] found an acceleration in degradation rate for the sonication of poly(alkyl methacrylates) in systems with higher Flory - Huggins interaction parameters. (a higher value indicates that the polymer chain is more uncoiled). Similar observations have been made by other workers.[172]

Temperature

Several studies of degradation over a temperature range have been carried out, for example, Thomas and Alexander[173] studied the sonication of cellulose nitrate in a series of acetate solvents between 0°C and 25°C, Schmid and Beuttenmuller[174] looked at the sonication of polystyrene in toluene over the temperature range 40°C to 120°C. All of these results showed lower rates of degradation and a higher $M_{lim.}$ at the higher temperatures.

Applied pressure

Decreases in the rate of degradation have been observed by Schmid and Rommel[156] and by Brett and Jellinek[175] upon application of pressure. The nature in which the pressure was applied was also found to be important. When pressure was applied to prevent the formation of cavities by increasing the gaseous pressure over the solutions being sonicated, it was observed that degradation decreased, however, it couldn't be prevented. When pressure was applied with a mercury column, however, a rapid decrease to zero degradation was observed. The reason for these observed differences is that when applied as an increase in the amount of gas in the system, the increase in pressure was suppressing the cavitation, however, the increased concentration of gas which dissolved in the solvent counteracted this.

Dissolved gases

Very little work has been described on the effect of dissolved gases on degradation processes, however, the work attempting to investigate the effect of applied pressure gives an indication of what happens. It has also been found that the

presence of more soluble gases in a system result in a lower rate of degradation and also a higher value for M_{lim}.[176]

Other, additional factors which affect degradation have also been observed.

Polymer molar mass

Degradation has been found to be greater for higher initial molar masses and the value of M_{lim} has been found to be independent of this property[177]

Concentration of the solution

All observations have shown that as the concentration of the solution being sonicated was increased, the rate of degradation decreased. Gooberman and Lamb[162] have found that a maximum rate constant was observed in the 0.01% - 0.03% (w/v) range and that the rate fell at higher concentrations. This decrease has also been observed by other workers.[172,178]

Nature of the polymer

Several workers[161] have found that the chemical nature of the polymer is unimportant (i.e. similar values for the rate of degradation and for M_{lim} were observed for different polymers), however, the presence of weak links in a chain has been found to affect the degradation. Encina et al.[179] found that poly(vinyl pyrollidone) with some peroxide linkages in the chain degraded faster and gave a lower Mlim than did the homopolymer. The recovered polymer had the molar mass which would be expected if all of the peroxide links had broken.

1.11.4 MECHANISM OF ULTRASONIC DEGRADATION

Early mechanisms which were proposed for ultrasonic degradation did not consider cavitation to be of importance, instead they assumed that frictional and impact forces between polymer and solvent molecules were sufficiently developed to be responsible for the bond cleavage. Schmid and Rommel[156] showed that degradation was not a result of oxidative fission caused by a combination of the atmosphere and the ultrasound by performing sonications under both air and nitrogen atmospheres, the same degradation rate was observed in both. Schmid[180] proposed that frictional forces, exerted by an oscillating solvent, were of the right order of magnitude to break C-C bonds in a polymer. If this mechanism was correct it would be reasonable to assume that degradation would cease if the solute and solvent were of the same density, however, when solutions of polystyrene in carbon tetrachloride - toluene

mixtures were sonicated no difference in degradation was observed.[170,174] Other early ideas were proposed by Jellinek and White,[181] who suggested collisions between polymer molecules and solvent molecules and Thieme[182] who suggested macromolecular collisions.

The overwhelming evidence now points to cavitation being responsible for degradation. Three general ideas have emerged;

a) thermal effects due to hot spots created in the bubble[133]

This mechanism can generally be discounted because of observed differences between ultrasonic and thermal degradations and also because of the fact that the polymer chains would be insufficiently volatile to enter the bubbles where these effects occur.

b) shock waves produced from transient bubble collapse[183]

Several ideas have emerged about what effect these shock waves would have on the macromolecules and how they might lead to degradation. For example, Gooberman[184] said that degradation was a result of the changes in pressure experienced upon cavitational collapse. During the pressure rise created by a growing bubble the macromolecule is compressed. The number of solvent molecules within the volume of this compressed macromolecule will also be greater when the pressure is at its peak value than at atmospheric pressure. Upon collapse, an exponential pressure drop is experienced which causes the solvent molecules to flow out of the macromolecule, this flow sets up stresses in the macromolecule which eventually lead to degradation.

Another idea was suggested by Thomas[183] who proposed that cavitational collapse resulted in large hydrodynamic pressures and velocity gradients in the surrounding fluid.[136,144] If sufficiently large velocity gradients exist across the volume of a macromolecule then it will distort along a radius of the collapsing cavity and stresses will operate on that molecule. Thomas assumed that solution concentrations were moderately low so that polymer entanglements could be discounted.

c) shear forces from pulsating, stable cavitation

When a polymer is subjected to hydrodynamic shear, centre cleavage of the macromolecules is known to occur.[185] Similarly it was thought that shear stresses arising from rapid movements around pulsating, stable cavitation bubbles would be sufficient to cause degradation.[186]

As yet, there is no clear agreement as to which degradation mechanism is in operation, the generally accepted idea is that degradation is caused by a combination of the effects which have been observed.

1.11.5 THE EFFECT OF CHAIN CLEAVAGE

When a covalent bond is broken two possibilities exist;
- i) homolytic fission which results in two macroradicals, or,
- ii) heterolytic fission which results in two macromolecular ions.

In the ultrasonic cleavage of bonds the formation of macromolecular radicals is most commonly (but not exclusively) observed. The first evidence for this was presented by Melville and Murray[153] who sonicated solutions of polymers in the presence of vinyl monomers. Henglein[187] used 2,2'-diphenylpicrylhydrazyl, (DPPH), as a radical scavenger and Tabata et al.[188] observed macroradicals by ESR in the sonication of polystyrene, poly(methyl methacrylate), polypropylene and poly(vinyl acetate).

Macromolecular ions were observed by Thomas and de Vries[189] when poly(dimethylsiloxane) was sonicated in the presence of ^{14}C methanol. The radioactivity was incorporated into the polymer upon sonication, but, was not when poly(dimethylsiloxane) solutions were refluxed.

It was shown earlier that polyphosphazenes, by virtue of the vast array of side groups available, are a very versatile class of material. However, because of the reactive nature of the 'unsubstituted' polymers, the synthetic procedures needed to produce useful materials can often be very complex and involved. Ultrasound has been shown to be a very useful tool in the synthesis and modification of a great many polymer systems and also in the modification of more conventional chemical reactions. It was the aim of this work to investigate whether these two areas of chemistry could be combined in order to increase the ease with which the polyphosphazenes could be either synthesised or processed by first looking at the small molecule phosphazene chemistry and then by progressing to the polymer systems.

As can be appreciated, from the previous discussion of phosphazene chemistry, a great many reactions of this type of material can be very complex and not all of those observable at a small molecule level are able to be efficiently transferred to a high polymer level. For this reason the work carried out began with a number of small molecule systems in order to try to decide which would be the most suitable to carry

forward to study at the high polymer level. This initially took the form of looking at a previously known, well characterised system in order to adequately compare data from both thermal and ultrasonically controlled reactions before progressing to novel systems. This would enable any effects of the applied ultrasound to be detected and explained more easily. The choice of the novel systems was led to some extent by the brief given by the sponsors of the project who had expressed a wish to develop polyphosphazenes bearing side groups that possessed the ability to undergo further reaction.

Once suitable small molecule systems had been found, and any effect of ultrasound on these systems investigated, a suitable synthetic route to the high polymer equivalents was sought. This process involved searching for the most suitable synthetic method for the synthesis of the polyphosphazenes being studied and also for the most practical way in which to apply ultrasound to the synthetic procedures being used.

The final component of the project involved investigation of the effect of ultrasound on pre-prepared samples of polyphosphazenes: this included looking at the effect upon molecular weights, molecular weight distributions, some of the basic physical properties of the polymers and also an initial investigation into the suitability of a variety of ultrasonic degradation rate models for describing the effects of ultrasound on polyphosphazene systems.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

Hexachlorocyclotriphosphazene, $P_3N_3Cl_6$, 99+%	(Nippon Shoji Co. Ltd, Japan)
p-Cresol, $HO(C_6H_4CH_3)$, 99%	(Aldrich)
2,4,6-Tri-t-butylphenol, $HO[C_6H_2(C_4H_9)_3]$, (96%)	(BDH)
Sodium metal, 99%	(Aldrich)
Tetrabutylammonium bromide, Bu_4NBr, 99%	(Aldrich)
THF, C_4H_8O, 99+%,HPLC grade	(Aldrich)
Toluene, $C_6H_5CH_3$, 99+%	(Aldrich)
Sodium hydroxide, NaOH, pellets 97%	(Aldrich)
Hydrochloric acid, HCl, 2.0M	(Aldrich)
Glycidol, HOC_3H_5O, (96%)	(Aldrich)
Sodium carbonate, anhydrous, (99.5+%)	(Fisons)
Trifluoroethanol, $HOC_2H_2F_3$, (99+%)	(Aldrich)
Dimethylformamide, $(CH_3)_2NCO$, (99%)	(Aldrich)
Phenylmagnesium chloride, PhMgCl, (2.0M in THF)	(Aldrich)
t-Butylmagnesium chloride, BuMgCl, (2.0M in THF)	(Aldrich)
1,2,4-Trichlorobenzene, $C_6H_3Cl_3$, (99%)	(Aldrich)
Sulphamic acid, H_2NSO_3H, (99+%)	(Aldrich)
Calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$, (98%)	(Aldrich)
Hexane, C_6H_{14}, 95+%, HPLC Grade	(Aldrich)
Ethanol, C_2H_5OH, (95%)	(Aldrich)
Benzoic acid, C_6H_5COOH, 99%	(Aldrich)
Chlorobenzene, C_6H_5Cl, 99.6%	(Aldrich)
Heptane, C_7H_{16}, 99%	(Aldrich)

All solvents were purified by standard techniques. $P_3N_3Cl_6$ was dried under vacuum at 50°C for several hours prior to use in order to remove all moisture. Glycidol, (Hydroxymethyl)oxirane, was purified by vacuum distillation.

All other materials were used as supplied.

2.2 ANALYTICAL TECHNIQUES / APPARATUS

NMR measurements were made on a JEOL GX400, 400MHz spectrometer. ^{31}P NMR was carried out in either $CDCl_3$ solution or THF/$CDCl_3$ solutions with 85%

H_3PO_4 as an external chemical shift reference. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution with TMS as an internal chemical shift reference.

IR spectra were recorded on a Perkin Elmer 983 spectrophotometer either in solution or as KBr disks.

Gel Permeation Chromatography of polymer samples was carried out on a Bruker LC41 chromatograph linked to an Epson QX16 data station with a PLGel, mixed bed, 60cm, 10mm i.d. column and a RI detector. The eluent was THF containing 0.1 wt.% Bu_4NBr as an ionic species. The samples were run as 0.1% solutions at a flow rate of 1.0 cm^3min^{-1} and were compared to low polydispersity polystyrene standards (supplied by Polymer Labs. Ltd.). Molecular weights of the standards ranged from 1050 to 2,650,000.

Differential Scanning Calorimetry was carried out using a Dupont 910 module with data analysis by a Dupont 9900 system. Indium and water calibrations were used.

Three types of ultrasonic sources were used;

i) A Kerry Ultrasonics pulsatron 325 cleaning bath.

ii) A VC50 ultrasonic probe with a horn diameter of 6mm operating at a frequency of 23kHz

iii) A VC600, Sonics and Materials Ltd., ultrasonic probe with a horn diameter of 12mm operating at a frequency of 23kHz.

2.3 SMALL MOLECULE (CYCLIC) SYSTEMS

2.3.1 PREPARATION OF SODIUM ALKYL/ARYLOXIDES.

Freshly cut sodium metal was slowly added to a solution of the particular reagent to be used in anhydrous THF. The mixture was then stirred under an atmosphere of dry N_2 until all of the sodium had reacted. Heating was applied where necessary.

The resulting solutions were used immediately in the subsequent reactions with $P_3N_3Cl_6$.

2.3.2 REACTION OF SODIUM ALKYL/ARYLOXIDES WITH $P_3N_3Cl_6$.

The same general procedure, which was based upon that used by Karthikeyan and Krishnamurthy[45], was carried out for several of the reactions (these are listed in table 2.1). A typical procedure was that used in the 1:1 reaction of sodium p-cresoxide with $P_3N_3Cl_6$ in anhydrous THF.

A solution of sodium p-cresoxide (0.005 moles) in anhydrous THF was added dropwise to a well stirred solution of $P_3N_3Cl_6$, (1.74g, 0.005 moles), in anhydrous THF (20 - 25 cm^3) at room temperature and under an atmosphere of dry N_2. The mixture was then allowed to react at 25°C for 30 hrs.

After the alloted time, the THF was removed by vacuum distillation and the mixture was dissolved in diethyl ether. This solution was filtered to remove NaCl and washed with 5% (w/w) NaOH solution (2 x 25cm^3), 0.2M HCl (2 x 25cm^3) and water (3 x 25cm^3). After drying over $MgSO_4$ the solvent was removed to yield the product mixture.

The various reaction conditions used for the different reagents are listed in Table 2.1

Table 2.1

Reagent	Stoichiometry	Amount Na	Amount HOAr	Reaction Temp.	Reaction time
p-cresol	1:1	0.119g	0.621g	25°C	30hr
	1:2	0.232g	1.241g	25°C	40hr
	1:6	1.150g	6.030g	60°C	60hr
Trifluoroethanol	1:1[a]	0.118g	0.52g	25°C	30hr
	1:6	0.697g	3.10g	60°C	60hr
2,4,6-Tri-t-butylphenol	1:1	0.118g	1.334g	25°C	30hr
	1:3	0.35g	3.96g	40°C	48hr
	1:6	0.697g	7.943g	60°C	60hr
	1:1[b]	0.118g	1.334g	25°C	30hr
Glycidol	1:1(c)	0.119g	0.38g	25°C	30hr
	1:6	0.697g	2.23g	40°C	60hr

Differences to the typical procedure.

(a) The trifluoroethanol system.

Prior to the commencement of the work up procedure any unreacted sodium trifluoroethoxide was neutralised by the addition of the reaction solution to water. This was essential as previously workers have found that attempts to isolate the sodium salt of trifluoroethanol have led only to adducts and ultimately to an explosion if all of the solvent was removed.[45] Products were then extracted with diethyl ether.

(b) The 2,4,6-tri-t-butylphenol system.

This reaction was carried out in the presence of Bu_4NBr, (0.01g), which was introduced to the solution of 2,4,6-tri-t-butylphenol prior to the addition of the sodium metal.

(c) The glycidol system.

The work up procedure for this reaction omitted the NaOH and the HCl washes.

2.3.3 REACTIONS OF $P_3N_3Cl_6$ WITH ALKOXY/ARYLOXY REAGENTS USING Na_2CO_3 AS A HYDROGEN HALIDE ACCEPTOR.

A typical reaction procedure was that of the reaction of 2,4,6-tri-t-butylphenol with $P_3N_3Cl_6$ in 1:3 stoichiometry.

A solution of 2,4,6-tri-t-butylphenol, (3.96g, 15 mmol), in anhydrous THF was slowly added to a well stirred mixture of Na_2CO_3, (3.22g, 30 mmol), and a solution of $P_3N_3Cl_6$, (1.74g, 5 mmol), in anhydrous THF. The resulting mixture was heated to 40°C and was stirred for 48hrs. under an atmosphere of dry N_2.

Upon completion, the reaction mixture was allowed to cool to room temperature and was filtered in order to remove NaCl and excess Na_2CO_3. The reaction solvent was then removed and the resulting solid dissolved in diethyl ether then filtered again if necessary. The solution was then washed with 5% (w/w) NaOH solution, (2 x 25cm^3), 0.2M HCl, (2 x 25cm^3) and water, (3 x 25cm^3). After drying over $MgSO_4$ the diethyl ether was removed to yield the product mixture.

The various reaction conditions used for the different reagents are listed in Table 2.2.

Table 2.2.

Reagent	Stoichiometry	Amount HOAr	Amount Na_2CO_3	Reaction Temp.	Reaction Time
Trifluoroethanol	1:1	0.52g	1.10g	25°C	30hr
	1:6	3.10g	6.35g	60°C	60hr
2,4,6-tri-t-butylphenol	1:1	1.35g	1.60g	25°C	30hr
	1:3	3.96g	3.22g	40°C	48hr
	1:6	8.10g	6.35g	60°C	60hr
Glycidol	1:1	0.38g	1.60g	25°C	30hr
	1:6	2.23g	6.36g	40°C	60hr

Differences to the typical procedure.

(a) The trifluoroethanol system.

Prior to the commencement of the work up procedure any unreacted trifluoroethanol was neutralised by the addition of the solution to water and then the products were extracted with diethyl ether.

(b) The 2,4,6-tri-t-butylphenol system.

This method was also attempted in different solvents, namely DMF and 1,4-dioxane. Both of these required vacuum distillation in order to remove the solvent during work up so as to prevent the degradation of any products formed.

In DMF the reaction temperature was initially reflux, (153°C), however, this proved to be too extreme and was altered to 80°C in later reactions.

(c) The glycidol system.

The work up procedure for these reactions ommitted the NaOH and HCl washes.

2.3.4 REACTIONS OF $P_3N_3Cl_6$ WITH N,N-DIMETHYLFORMAMIDE.

Either, a mixture of DMF in anhydrous THF, or an excess of DMF, was added slowly to a stirred solution of $P_3N_3Cl_6$, (1.74g), in anhydrous THF under an atmosphere of dry N_2 and was allowed to react under various conditions, (Table 2.5). Upon completion, any insoluble solid was filtered from the reaction mixture, was washed with THF and was kept.

The reaction mixture, along with the THF washings, was distilled under vacuum to remove the reaction solvent and the resulting solid was dried under vacuum to ensure removal of all DMF.

Table 2.3.

Stoichiometry	Solvent	Amount Na_2CO_3 *	Reaction Temp.	Reaction Time
Excess DMF	-	6.36g	25°C 80°C	60hr

* All reactions were carried out both with and without the presence of Na_2CO_3 in order to see if this was an influencing factor on the reaction.

2.3.5 REACTION OF $P_3N_3Cl_6$ WITH GRIGNARD REAGENTS.

The same procedure was used for all Grignard reagents used.

Typically, a solution of $P_3N_3Cl_6$, (1.74g), in anhydrous THF was cooled to 0°C, under an atmosphere of dry N_2. PhMgCl, (2.0M in THF), was then added dropwise to the solution. After each 0.5 equivalent, ($1.25cm^3$) had been added the mixture was stirred for one hour before any further addition took place. After addition of all of the Grignard, (1 equivalent), the mixture was stirred for 24hr. under an atmosphere of dry N_2 while the temperature was maintained at 0°C.

1ml samples were taken at various times throughout the reaction and were quenched by the addition of isopropyl alcohol, ($3cm^3$). Any resulting precipitate was filtered off and the samples were submitted for ^{31}P NMR analysis.
Samples were taken at 1, 2, 3, 6, 11, 20 and 26 hours of the reaction.

Reactions with t-BuMgCl were carried out in an identical manner.

2.4 POLYMERISATION REACTIONS.

2.4.1 BULK POLYMERISATIONS

These reactions were carried out as described by Allcock *et al.*[14]

$P_3N_3Cl_6$, (2.0g, 5.7 mmol), was placed in a $10cm^3$ polymerisation ampoule which was then evacuated for 30 minutes at approximately 0.1 mm Hg. The ampoule was then isolated from the vacuum and its contents heated until molten and then cooled until they resolidified. This process was repeated with the ampoule being opened to the vacuum between each melt - freeze cycle in order to remove any trapped air. The system was then evacuated for a further 30 minutes before the ampoule was sealed.

The sealed ampoule was placed in an oven at 250°C and was left for 48hr. Upon cooling, the tube was opened and the contents were dissolved in either toluene or THF. This solution was then poured into an excess of cold n-heptane in order to precipitate any polymer which had been formed.

2.4.2 SOLUTION POLYMERISATIONS.

Method 1

This method was also described by Allcock *et al*[14] and is very similar to that used in the bulk polymerisation.

$P_3N_3Cl_6$, (2.0g, 5.7 mmol), was placed in a polymerisation ampoule and was distilled in freshly distilled chlorobenzene, (approximately 2.0cm^3), to give a 50% by weight monomer - solvent mixture. The system was evacuated and a series of freeze - thaw cycles were applied in order to remove trapped air. The tube was then sealed and placed in an oven at 230°C for 72hr.

Upon cooling, the ampoule was opened and the contents were dissolved in either toluene or THF. The resulting solution was then poured into an excess of cold n-heptane in order to precipitate any polymer which had been formed.

Catalysed polymerisations were carried out in the same way but with the addition of the appropriate catalyst, either ethanol (2.6mg / g of $P_3N_3Cl_6$) or benzoic acid (10mg / g of $P_3N_3Cl_6$), prior to degassing.

Method 2

This method was based upon that described by Magill *et al.*[190]

A two-necked, round bottomed flask equipped with a condenser, was thoroughly dried and was flushed with dry N_2 while being heated to 100°C. $P_3N_3Cl_6$, (25g, 72 mmol), calcium sulphate dihydrate, (62mg, 0.36 mmol) and sulphamic acid, (65mg, 0.67 mmol) were added to the flask upon cooling and these too were flushed with dry N_2. 1,2,4-Trichlorobenzene solvent was then added to the flask. The resulting mixture was stirred at 216°C until the solution was seen to increase in viscosity (typically 1.5 - 2hrs.). The solution was then allowed to cool to approximately 50°C and was poured into an excess of cold hexane in order to precipitate the brown, elastomeric poly(dichlorophosphazene), (typically 10 - 12g). This precipitate was stirred in the hexane for at least 30 minutes in order to remove all occluded, unreacted $P_3N_3Cl_6$. The hexane was next decanted off and the poly(dichlorophosphazene) dissolved in the minimum amount of anhydrous THF. The resulting polymer solution (with any insoluble material filtered off) was then generally used immediately in a substitution reaction.

During the polymerisation process care was taken to ensure that all manipulations of the polymer were caried out under a stream of dry N_2.

2.4.3 SUBSTITUTION OF POLYDICHLOROPHOSPHAZENE.

The same general procedure was carried out for all attempted substitutions.

A typical reaction was that of the p-cresol substitution. Sodium metal, (5.93g, 0.26 mol), was added slowly to a solution of p-cresol, (27.9g, 0.26 mol), in anhydrous THF, with stirring and under an atmosphere of dry N_2. This mixture was then warmed

carefully until all of the sodium metal had reacted. To this solution was added, slowly, a solution of poly(dichlorophosphazene), (10 - 12g) in anhydrous THF, (20 - 30cm^3), and the resulting mixture was stirred at room temperature for 1hr before being heated to reflux for 48hrs.

The substituted polymer was purified by precipitation into an excess of cold water, followed by redissolution into THF (this cycle was continued until the water was no longer discoloured) and finally by precipitation into cold hexane. Each time, the precipitated polymer was stirred for at least 30 minutes in the non-solvent. The polymer thus obtained, (typically 8 - 10g) was dried under vacuum for at least 48hrs.

Table 2.4 shows the reaction conditions employed for the substitution of polydichlorophosphazene by various reagents.

Table 2.4.

Substituent	Amount HOAr[a]	Amount Na	Amount Na_2CO_3 [b]
p-cresol	27.9g	5.93	-
	27.9g	-	27.35
Trifluoroethanol [c]	25.8	5.93	-
	25.8	-	27.35

(a) Amounts of reagents used were based upon 15g of $P_3N_3Cl_6$ being converted to polymer so as to give an excess of reagent to ensure full substitution.

(b) The reactions were also carried out using Na_2CO_3 as a hydrogen halide acceptor instead of using the sodium salt of the alkyl/aryloxide.

(c) Prior to precipitation of the trifluoroethoxy polymer (into acetone rather than water in this case) any unreacted trifluoroethoxide was neutralised by the acidification of the reaction mixture by slow addition of concentrated HCl.

2.4.4 PREPARATION OF A PRE-SUBSTITUTED POLYMER.

This method was as described by Montague and Matyjaszewski.[113]

Preparation of the monomer.

A three-necked, round bottomed flask was set up with a condenser and an addition funnel and was flushed with dry N_2. The flask was charged with freshly distilled Tris(trifluoroethoxy)phosphite (17.2cm^3, 78 mmol) and was then cooled to 0°C. Freshly distilled trimethylsilyl azide (10.4cm^3, 78 mmol) was then added dropwise, with stirring to the phosphite.

The mixture was allowed to warm to room temperature and was then heated to 120°C, until bubbles of N_2 were seen to be evolved, followed by reflux for 24hrs under dark conditions. Upon cooling to 0°C a further 1 equivalent of trimethylsilylazide (10.4cm^3, 78 mmol) was added dropwise to the solution which was then heated to reflux for a further 24hrs. Upon cooling to 0°C a final 1.1 equivalent of trimethylsilylazide (11.7cm^3, 88 mmol) was added slowly to the mixture which was then heated to 120°C for a final period of 24hrs.

The resulting clear amber liquid was vacuum distilled to give two clear, colourless fractions; the first, distilling at 62 - 63°C (~ 10mm Hg) being unreacted trimethylsilylazide and the second, distilling at 72 - 74°C, being the desired polymerisation monomer, P-tris(trifluoroethoxy)-N-(trimethylsilyl)phosphinimine.

Polymerisation of the monomer.

A sample of the phosphinimine (4.3g, 10 mmol) was combined with 100µl of a 1M solution of n-Bu_4NBr in anhydrous THF in a flask equipped with a condenser and a dry N_2 purge. The mixture was then heated to 95°C (one reaction was also carried out at 35°C) for 1.5hr. and was then allowed to cool.

The resulting white solid was dissolved in anhydrous THF and this solution was poured into an excess of cold chloroform in order to precipitate the desired polymer. The polymer was collected by filtration and was dried under vacuum.

2.5 ULTRASONIC REACTIONS

2.5.1 CYCLIC SYSTEMS

Ultrasound was applied to the different polymerisation systems in one of two ways, (a) by the use of an ultrasonic bath, or (b) by the use of an ultrasonic probe

(a) The ultrasonic bath.

The same basic procedure was used for all of the systems.

Reagents were prepared in the same manner as described for the conventional reactions (Sections 2.4.1 - 2.4.5) and these were added slowly to a solution of $P_3N_3Cl_6$ (1.74g, 5 mmol) in anhydrous THF in a reaction vessel held in an ultrasonic bath. When addition was complete the ultrasound was switched on.

When the appropriate amount of time had elapsed the ultrasound was switched off and all subsequent procedures were as have been described previously.

Table 2.5

Reaction	Relevant table of conditions
1:1 $P_3N_3Cl_6$ + p-cresol	2.3
1:1 $P_3N_3Cl_6$ + trifluoroethanol	2.3
1:1 $P_3N_3Cl_6$ + glycidol	2.4
1:6 $P_3N_3Cl_6$ + glycidol	2.4
1:1 $P_3N_3Cl_6$ + PhMgCl [a]	Section 2.4.5

a For the reactions with the Grignard reagents the ultrasound was switched on after the addition of the first 0.5 equivalents of reactant and the reaction allowed to proceed for one hour before any further addition took place, just as in the conventional reaction.

(b) The ultrasonic probe.

In all reactions carried out in the cyclic systems the VC50 ultrasonic probe was used. A solution of $P_3N_3Cl_6$ (1.74g, 5 mmol) in anhydrous THF was introduced into an ultrasonic cell (Figure 2.1) and was degassed by bubbling dry N_2 through it for approximately 30 minutes. At the same time a solution of the substitution reagent in anhydrous THF was degassed in the same way. The reactant solution was slowly added to the $P_3N_3Cl_6$ solution by means of a gas tight syringe. When the addition was complete the ultrasonic probe was switched on. After the appropriate amount of time had passed the probe was switched off and all subsequent procedures were as have been previously described.

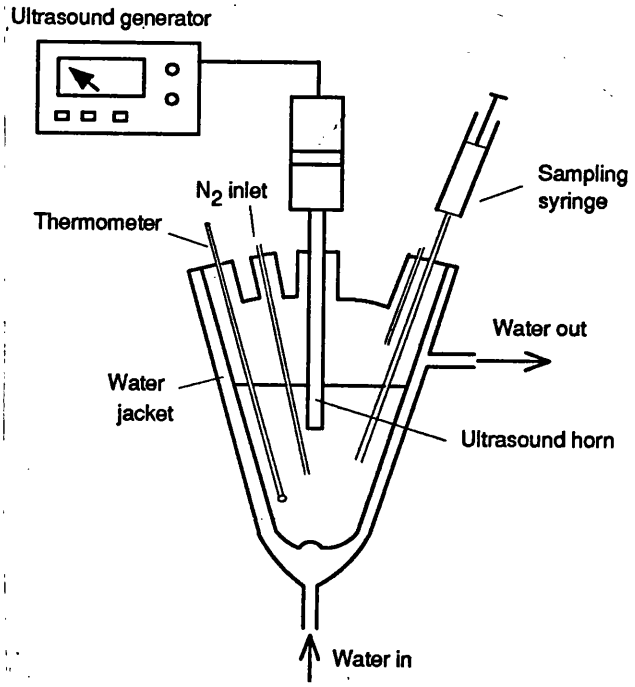


Figure 2.1 Diagram of an ultrasonic cell.

Table 2.6

Reaction	Relevant table	Ultrasound generator setting	Intensity (Wcm^{-2})[a]
$P_3N_3Cl_6$ + p-cresoxide	2.3	5	47.8
$P_3N_3Cl_6$ + trifluoroethoxide	2.3	5	47.8
$P_3N_3Cl_6$ + trifluoroethanol	2.4	5	47.8
$P_3N_3Cl_6$ + glycidol	2.4	5	47.8

(a) For an explanation of the conversion of generator setting to intensity see section 2.6

2.5.2 ULTRASONIC POLYMER SYNTHESIS.

Besides the practical difficulties of introducing ultrasound into a molten system (Section 5.5) at 250°C the very limited success of both of the ampoule polymerisation methods meant that ultrasound was applied to neither of them.

Solution polymerisation

A three-necked, round bottomed flask equipped with a condenser was thoroughly dried and was flushed with dry N_2 while being heated to 100°C. $P_3N_3Cl_6$, (25g, 72 mmol) calcium sulphate dihydrate, (62mg, 0.36 mmol) and sulphamic acid, (65mg, 0.67 mmol) were added to the flask and these too were flushed with dry N_2. 1,2,4-Trichlorobenzene ($20cm^3$) was then added to the flask.

At this point the VC600 ultrasonic probe, fitted with a 10cm extension bar, was fitted so that the probe tip was approximately 1cm from the bottom of the flask. The solution was then heated to either 25, 100 or 216°C and the probe switched on for 2hrs.

All subsequent procedures were as described previously. (Section 2.4.2)

Condensation polymerisation

The P-tris(trifluoroethoxy)-N-(trimethylsilyl)phosphinimine monomer was prepared as described in section 2.4.4 and was divided into two equal samples, (2.1g, 5 mmol each), one of which was combined with 50µl of a 1M solution of n-Bu_4NBr in anhydrous THF. Both samples were then placed in flasks equipped with a condenser and a dry N_2 purge. The flasks were immersed in an ultrasonic bath and were sonicated at room temperature for 1.5 hrs.

All subsequent procedures were as have been described in section 2.4.4.

2.5.3 DEGRADATION REACTIONS.

All experiments were carried out using the same general procedure.

A solution of the polymer in anhydrous THF, (0.5% (w/v) for the intensity studies, varying for the concentration studies) was deoxygenated in an ultrasonic cell (Figure 2.2), which was equipped with a thermocouple and a nitrogen inlet and outlet, by bubbling dry N_2 through it for 30 minutes. The appropriate conditions were set (the ultrasonic generator setting , for example) and the ultrasound was switched on.

Samples, ($1cm^3$), were taken from the cell at various times throughout the experiment for GPC analysis. After an appropriate amount of time had elapsed the ultrasound was switched off, the solution was concentrated and was precipitated into cold hexane in order to retrieve the polymer.

The various reaction conditions used are listed in Table 2.7.

Table 2.7.

Solution concentration (w/v)	Generator setting	Intensity (Wcm^{-2})
5%	5	47.8
1%	5	47.8
0.5%	5	47.8
0.1%	5	47.8
0.5%	1	14.1
0.5%	3	32.2
0.5%	5	47.8
0.5%	7	67.3
0.5%	10	94.6

2.6 CALIBRATION OF THE ULTRASOUND PROBES.

Various methods of determining ultrasonic power are available, for example; - i) the nominal power quoted by the manufacturers, which is usually related to the amount of energy supplied to the transducer and hence bears no real relationship to the energy actually transfered to the reaction system, could be used, or,

- ii) A calorimetric method in which a value is stated based upon the time taken to heat a known volume of distilled water through a measured temperature rise. The heat capacity of the reaction vessel is accounted for and so values for the ultrasonic power determined by this method can be compared with those calculated for other reaction systems / vessels.

The calorimetric method was used in this work.

A jacketed glass vessel was set up as for a sonication experiment (Figure 2.2) and was equipped with an electronic heater (a resistor) and a thermocouple. 100 cm^3 of distilled water was put into the vessel and was allowed to equilibrate to room temperature, a note of this initial temperature was made. The heater was then switched on and the temperature of the system was noted at regular intervals. The current through the heater and the voltage were measured using a multimeter.

This process was repeated with a new batch of water and with the ultrasonic probe acting as the heater and the temperature rise was monitored over the same time period as for the electric heating.

Results are shown in Table 2.8 and Figure 2.2.

Table 2.8

Time (s)	Temperature (°C)					
		Ultrasonic Generator Setting				
	Electric	1	3	5	7	10
0	17.3	17.5	17.5	17.5	17.5	17.5
30	18.3	19.1	19.8	20.7	22.3	23.9
60	19.3	19.6	21.4	23.3	25.8	28.9
90	20.0	20.0	22.8	25.7	28.7	33.7
120	20.8	20.6	23.8	27.4	31.4	37.9
150	21.7	20.9	25.0	29.4	34.1	41.4
180	22.2	21.2	26.2	30.8	36.2	44.2
210	22.9	21.8	27.0	32.2	38.0	46.7
240	23.4	22.1	27.9	33.1	39.5	49.0
270	24.1	22.2	28.8	34.4	41.0	51.0
300	24.6	22.7	29.4	35.2	42.4	52.5

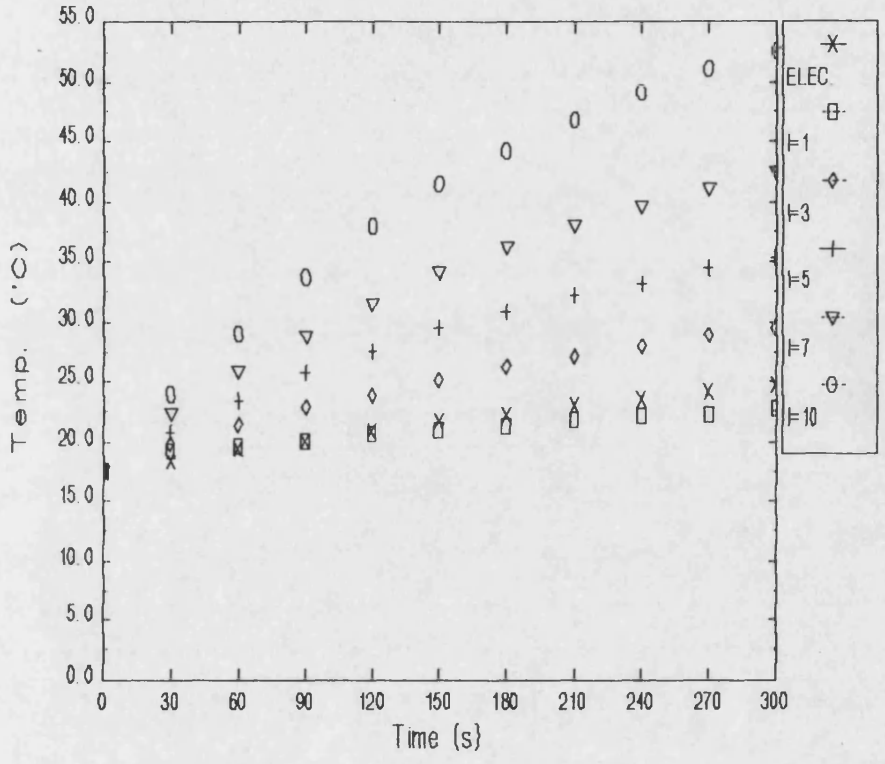


Figure 2.2 : Calibration of the VC600 ultrasonic probe.

The calculation

The energy supplied to the heater was calculated from

$$E=VIt$$

where V is the voltage, I is the current and t is the time in seconds. The heat capacity, c, of the system was obtained from the temperature rise of the system and if c is assumed to be constant for the experiments then heat losses to the surroundings can be ignored.

$$E=c\Delta\theta$$

where E is the energy supplied by the heater and $\Delta\theta$ is the measured temperature rise. The ultrasonic power supplied by the probe can now be calculated using

$$P=VI=c\Delta\theta/t$$

If the area of the probe tip is known then the ultrasonic intensity, or the power per unit area, provided by the probe can be calculated.

For example, for the generator setting of 5
A temperature rise of 7.3°C over 300s was noted for electrical heating.
Voltage, V = 12.43V
Current, I = 1.246A
Hence the heat capacity c = 636.5 JK^{-1}

A temperature rise of 17.7°C was noted over a time of 300s for ultrasonic heating.
Hence the power supplied by the probe, P = 37.55W

The area of the probe tip (taken from the manufacturers specifications) = 0.7853cm^2
Hence the ultrasonic intensity for a generator setting of 5 = 47.8Wcm^{-2}.

Consideration of errors.

The errors in the various parameters which were measured were estimated to be

Temperature	± 0.1°C	Voltage	± 0.01V
Time	± 1s	Current	± 0.01A

Hence, for the above calculation, the error in calculating the energy supplied to the heater is

$$\pm\left(\frac{0.01}{12.43}+\frac{0.01}{1.246}+\frac{1}{300}\right)x100\%$$

$$\underline{=\pm 1.22\%}$$

The error in measuring $\Delta\theta$ for the electrical heating is

$$\pm\left(\frac{0.1}{17.3}+\frac{0.1}{24.6}\right)x100\%$$

$$\underline{=\pm 1\%}$$

The error in calculating the heat capacity, c, is therefore

$$\pm(1+1.22)\%$$

$$\underline{=\pm 2.22\%}$$

The error in measuring $\Delta\theta$ for the ultrasonic heating is

$$\pm\left(\frac{0.1}{17.3}+\frac{0.1}{35.2}\right)x100\%$$

$$\underline{=\pm 0.86\%}$$

This means that the error in calculating the power supplied by the probe is

$$\pm 2.22+0.86+\left(\frac{1}{300}\right)x100\%$$

$$\underline{=\pm 3.41\%}$$

Since the area of the probe was obtained from the manufacturers specifications the resulting error in the ultrasonic intensity is also ± 3.41%. This means that for the generator setting of 5, I=47.8 (± 1.6) Wcm^{-2}

When the calculations for the remaining generator settings were carried out the results shown in Table 2.9 were obtained.

Table 2.9

Generator Setting	Intensity (Wcm^{-2})
1	14.1 (± 0.5)
3	32.2 (± 1.1)
5	47.8 (± 1.6)
7	67.3 (± 2.3)
10	94.6 (± 3.1)

The calibration of the smaller VC50 ultrasonic probe was carried out by following the same method but with only $50cm^3$ of water used rather than $100cm^3$. The intensity found for the generator setting of '50' (the only one used during these studies) was 25.4 (± 0.9) Wcm^{-2}.

CHAPTER 3

SUBSTITUTION REACTIONS OF CYCLIC PHOSPHAZENES

3.0 THERMAL REACTIONS OF $(NPCl_2)_3$ WITH VARIOUS NUCLEOPHILES.

To begin the study in this thesis it was decided to investigate reactions which had been previously described in the literature in order to gain an appreciation of the various techniques which would be needed upon advancement to more novel reactions. These initial studies would also provide a good data base upon which to begin a study of the effect of ultrasound on the reactions of cyclic phosphazenes. Once this had been done, previously unknown systems would be studied, including the synthesis of functionalised cyclic phosphazene systems which would have the potential for further reaction. It was envisaged that those systems which gave good results at the cyclic level would be repeated on the high polymer.

3.1 REACTIONS OF $P_3N_3Cl_6$ WITH p-CRESOL, (p-METHYLPHENOL).

This system was chosen as the initial reaction to be studied because of reasons already mentioned and also because of the good reported yields and variety of substitution patterns previously observed.[45a] A selection of reactions was chosen to be repeated and the products identified using ^{31}P NMR.

A number of different levels of substitution were observed along with various stereoisomers; the ^{31}P NMR data for the observed products is given in Table 3.1.1 and the product distribution in Table 3.1.2.

The results observed show a good comparison to those of Karthikeyan and Krishnamurthy[45a] and the same general trends are observed.

The reaction appears to follow a predominantly non-geminal pathway as would be expected for a weak electron donor like an aryloxy group. Stereoisomerism within the non-geminal materials was observed at the bis- and trisubstituted levels in the form of a second AX_2 spectrum at a slightly different chemical shift for the bisubstitution and as a set of overlapping peaks from an A_3 and an AB_2 spectrum for the trisubstituted product (Figure 3.1.1). For an explanation of the ^{31}P NMR used in these studies see Appendix 1.

Table 3.1.1: ^{31}P NMR data for the observed products in the p-cresol systems.[a]

Compound[b]	^{31}P Chemical shift (ppm.)			$^{2}J_{PNP}$ (Hz.)
	PCl_2	PCl(OAr)	$P(OAr)_2$	
trimer	19.93(s)			
monosub	22.32(d)	12.34(t)		60.0
bisub ng	24.68(t)	15.47(d)		63.5 - 65.5
	24.52(t)	15.29(d)		
bisub g	23.52(d)		-0.37(t)	63.5
trisub ng	18.4[c]	18.4[c]	18.4[c]	
trisub g	25.96(d)[d]	17.73(d)[d]	2.66(d)[d]	67.3 - 69.3
	25.54(d)	17.26(d)	2.20(d)	
hexasub			9.07(s)	

(a) (s) = singlet, (d) = doublet, (t) = triplet, g = geminal and ng = non-geminal

(b) See figure 1.6.1 for a diagram of the listed products.

(c) The signals for this material were overlapping, see text.

(d) The signals for this material were observed as doublets of doublets.

Table 3.1.2: Product distributions for the thermally controlled p-cresol reactions.

Stoichiometry	Compounds Observed	% of Total cyclic products	% Cyclic products in all
1:1	trimer	10.9	99.3
	monosub	75.6	
	bisub ng	13.5	
1:2	monosub	14.4	99.0
	bisub ng	76.1	
	bisub g	3.1	
	trisub ng	4.7	
	trisub g	1.7	
1:6	hexa	100	96.3

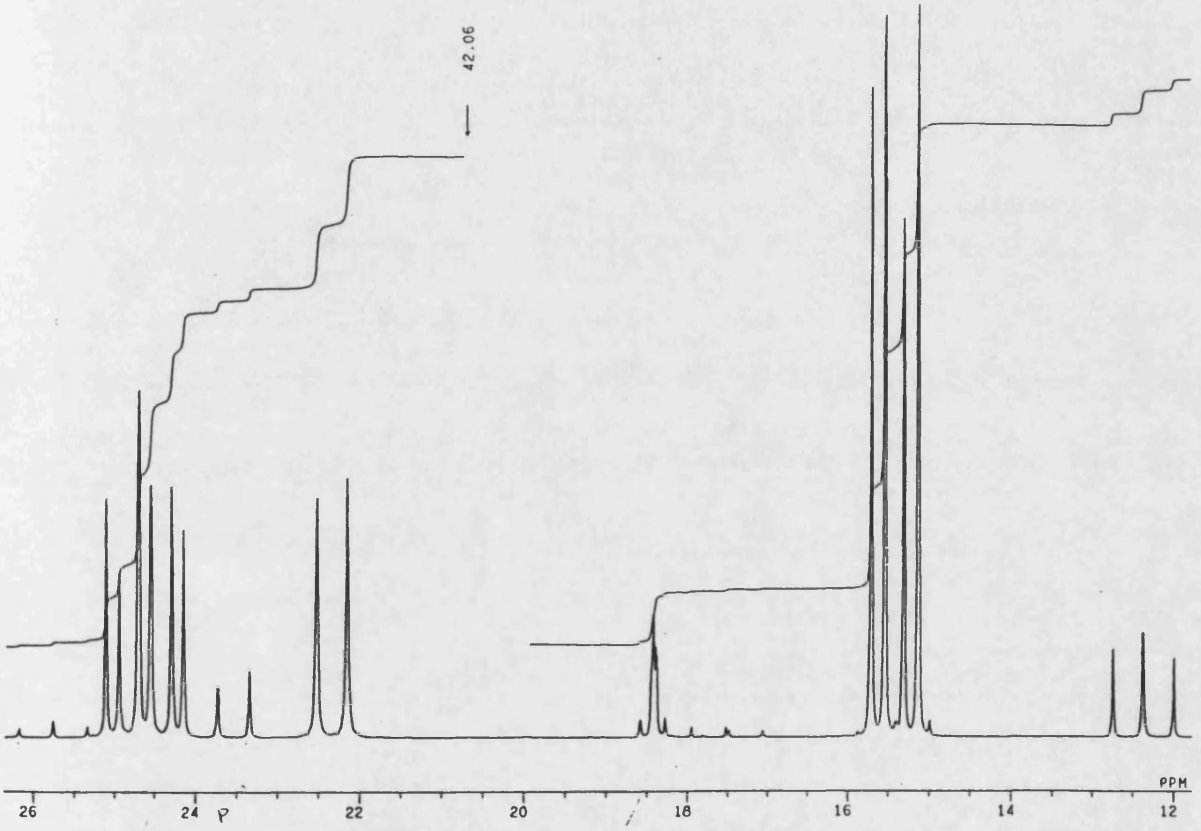


Figure 3.1.1: ^{31}P NMR showing stereoisomerism of the bi- and trisubstituted non-geminal p-cresol products.

The NMR data shown in table 3.1.1 matches closely that previously reported in the literature,[45a] with all values for the chemical shifts being within 1ppm of those reported. It has not been possible to distinguish between the different stereoisomers purely by analysis of the ^{31}P NMR data, however, it has been possible to estimate the proportions of these isomers present in the mixtures by looking at the integration of the spectra. It has been found that the cis and trans isomers are present in effectively equal amounts in the bisubstituted product.

The ^{31}P NMR data has been confirmed by GC-MS for which a sample from the 1:1 reaction was submitted. Four products were detected which were identified from their mass spectra as

- i) unreacted $P_3N_3Cl_6$, m/z = 347,
- ii) monosubstituted product, m/z = 419,
- iii) bisubstituted product, m/z = 491.

The bi-substituted product was further allocated as the non-geminal isomer due to two peaks being identified in the gas chromatogram, these being due to both cis and trans isomers which would not be present if this was the geminally substituted isomer (see figure 1.6.1). The relative proportions of these two signals were approximately 46% : 54%, thus adding to the evidence for the comparable formation of cis and trans isomers in this reaction, although it was not possible to assign the peaks to their isomer of origin.

Again, in common with the work of Karthikeyan and Krishnamurthy[45a], an effectively linear trend was observed when the observed chemical shifts were considered with respect to the level of substitution. (Figure 3.1.2) The ^{31}P shifts move downfield with an increasing level of substitution of the phosphazene ring, this is believed to be due to electron donation by the aryloxy groups. This would result in increased electron density at the substituted phosphorus and hence would lead to a slightly more positive environment at the unsubstituted phosphorus atoms relative to their environment prior to substitution of the ring. Deshielding, and hence a downfield shift, would result. This is also parallelled by an increase in the coupling constant $^2J_{PNP}$. These same trends have also been observed in other systems[45b].

The results obtained in these initial studies of the reaction of $P_3N_3Cl_6$ with p-cresol match closely those obtained by other workers[45a] and are as would be expected for the reaction of a weak electron donor with $P_3N_3Cl_6$ (section 1.6.2). The NMR data used to identify the various products is essentially identical and the observed products, although with slight differences in the relative distributions (all are generally within 10% of those previously reported), are the same. Trends in the NMR data observed by Krishnamurthy, such as the rise in ^{31}P NMR chemical shift values with increasing substitution level, have also been observed in this work. As such it is clear

that this work provides some good data upon which to base a study of the effect of ultrasound on this reaction.

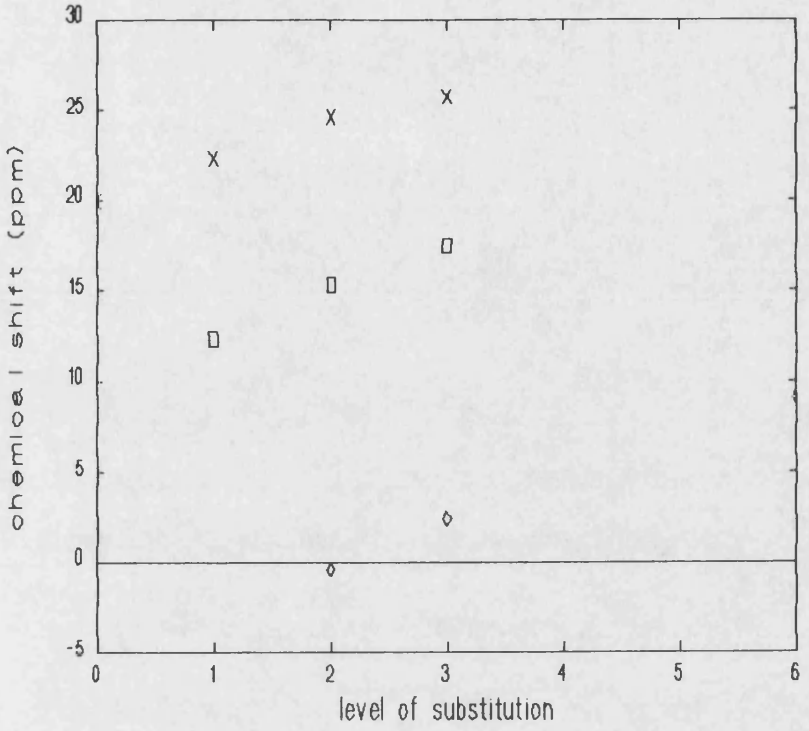


Figure 3.1.2: Relationship between substitution level and ^{31}P NMR chemical shift for the reaction products of $P_3N_3Cl_6$ with p-cresol.

3.2 REACTION OF $P_3N_3Cl_6$ WITH TRIFLUOROETHANOL

The reaction with trifluoroethanol was carried out as this too had previously been described in the literature[45b] and had readily available data to use as a comparison not only for the thermally controlled reactions, but, also for any ultrasonically controlled reactions which would be carried out. As in the p-cresol system, only a selection of reactions were carried out (1:1 and 1:6 stoichiometries only in this case) and the products identified using ^{31}P NMR. The results obtained, Table 3.2.1., show good comparison to the previously reported data. The chemical shift values for the identified products are within 1ppm of those previously reported and the product distributions are similar, generally within 10% of those in the literature. The main difference in the results obtained in this work being that a smaller range of substitution products was observed than is reported in the literature. This can be explained, however, by looking at the reaction stoichiometries, in the literature reaction a 1.4 : 1 ratio was used whereas in this work an exact 1 : 1 ratio was used, although not vastly

different this may be enough to result in the additional substitution products observed by Schmutz and Allcock[45b].

Table 3.2.1.

Compound	δPCl_2	$\delta PCl(OR)$	$^2J_{PP}$ (Hz.)
$P_3N_3Cl_6$	19.8ppm		
monosub.	21.9ppm	15.8ppm	64.0 - 66.0
bisub (ng) [a]	24.2ppm	18.4ppm	67.9 - 69.9

(a) This was assumed to be the non-geminal trans isomer of the bi-substituted product based upon the arguments presented by Schmutz and Allcock.[45b]

The product distribution for the identifiable products from this reaction is shown in Table 3.2.2.

Table 3.2.2.

Compounds Observed	% Products
$P_3N_3Cl_6$	40
monosubstituted	35
bi-substituted (ng)	20

As the reaction proceeded as expected with no real complications it was decided to look at what effect ultrasound would have on this system and also to use this reaction at the polymeric stage in order to learn the techniques which would be necessary in the synthesis of the 'unknown' polymeric systems.

3.0 REACTION WITH GRIGNARD REAGENTS

According to reports in the literature the reaction of $P_3N_3Cl_6$ with Grignard reagents is very complex (section 1.6.2). Initial studies led to the belief that ring-opened, acyclic materials were the major products from reaction[192], however, later work has suggested that cyclic, substitution products have been observed.

Allcock *et al.* report[66b] on a competition reaction between a nucleophilic substitution pathway, which yields mono-substituted organocyclophosphazenes, (VI), and a metal - halogen exchange pathway, which yields phosphorus linked bi(cyclophosphazenes), (VII), with little or no acyclic material observed. (scheme 3.3.1.) The relative proportions of these products are dependent upon the nature of the organic substituent group. For example, due to the steric bulk of the t-butyl group only the mono-substituted organophosphazene is observed when $P_3N_3Cl_6$ reacts with t-BuMgCl and only the bi(cyclophosphazene) when reaction is with PhMgCl. This is

due to the fact that the more planar Ph groups are able to adopt a conformation such that they can pack together so as to allow the formation of the bi(cyclophosphazene). The t-Butyl groups, however, are unable to do this and so the bi(cyclophosphazene) cannot form in this case.

These reactions were repeated in the manner described by Allcock[66b] and the ^{31}P NMR data for the products is shown in Table 3.3.1.

Table 3.3.1: ^{31}P NMR data for the expected products from reaction between $P_3N_3Cl_6$ and RMgCl (R = t-Bu or Ph)

Compound	^{31}P NMR Chemical shift (ppm.)			J (Hz.)
	δPCl_2	$\delta PCl(R)$	$\delta P(P)R$	
$P_3N_3Cl_6$	19.60			
$[P_3N_3Cl_4Ph]_2$	19.09		17.14	*
$P_3N_3Cl_5{}^tBu$	20.60	-12 - -13		~35.6

* No coupling constants could be measured from the spectrum for this species.

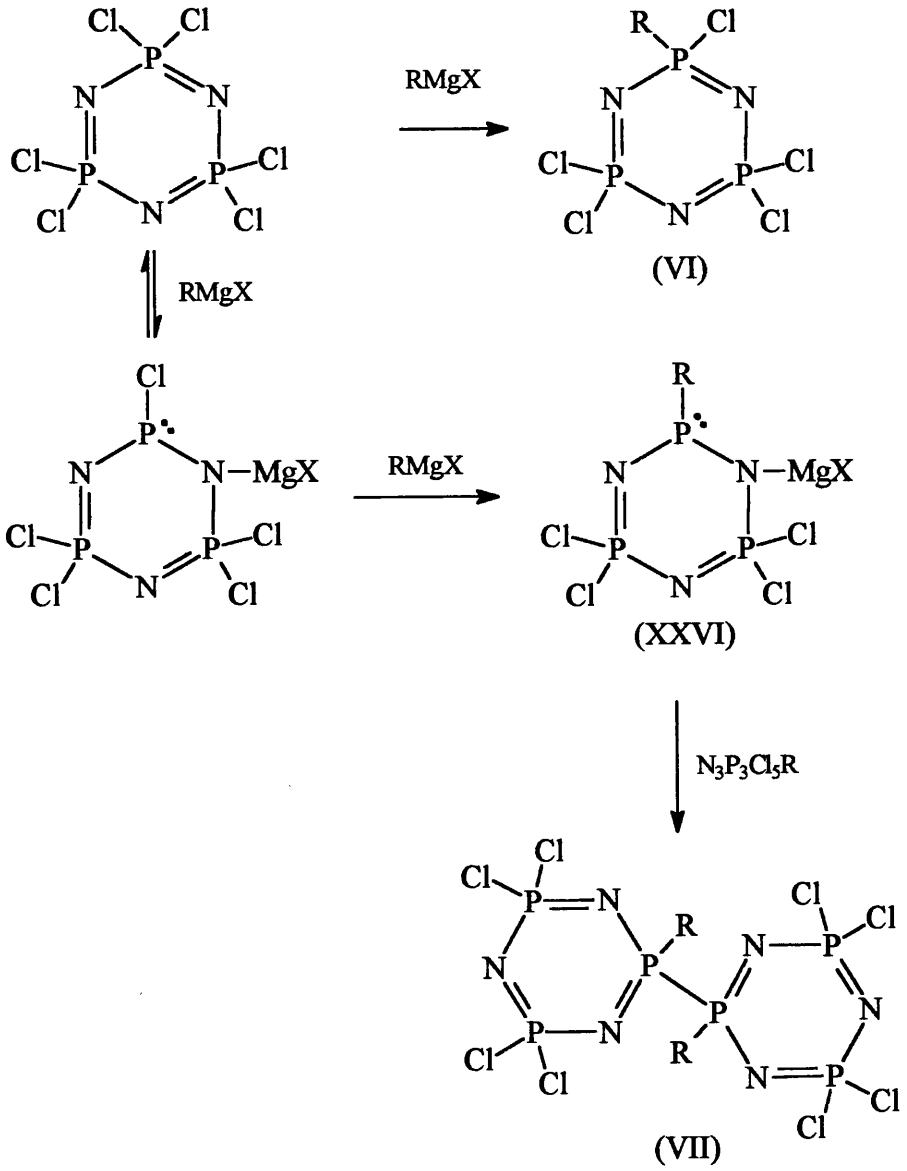
These are in good agreement with quoted literature values[66b].

In addition to these expected signals, however, other signals were observed in the spectra of both systems. These signals shared the same chemical shift values irrespective of the Grignard reagent used and are listed in Table 3.3.2.

Table 3.3.2: ^{31}P NMR data for the additional signals observed in the reaction between $P_3N_3Cl_6$ and RMgCl (R = t-Bu or Ph)

^{31}P NMR chemical shift (ppm)	multiplicity	J(Hz)
21.50	doublet	61.4
18.18	doublet	53.5
17.58	doublet	53.5
12.24	triplet	61.4 - 63.4
-7.96	triplet	53.5 - 55.5
-9.10	triplet	53.5 - 55.5

Scheme 3.3.1.

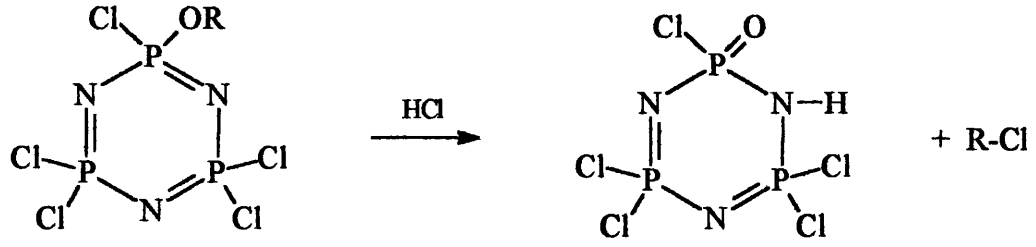


As the same signals are observed, irrespective of the Grignard reagent used, it is reasonable to assume that the materials which give rise to them must be free of the intended organo substituent. It would also seem likely that their source must be common to both reactions. The only proccess common to both systems which had the potential to give rise to further reaction was the method of quenching the reaction. In both instances 2-propanol (IPA) was added to the reactions in order to remove any excess, unreacted Grignard reagent prior to the analysis of the extracted samples.

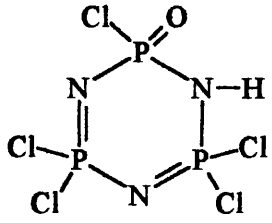
The reaction of IPA with cyclotetraphosphazene has previously been observed to result in substitution products when the IPA was intended as part of the purification procedure[15]. If unreacted $P_3N_3Cl_6$ was reacting with IPA one of the expected products would be the monosubstituted isopropoxyphosphazene. Literature values for the ^{31}P NMR chemical shifts of this material are given as 21.7ppm and 12.6ppm. (J = 62.7Hz.)[193], and compare well with the larger, AX_2 spectrum observed in the current study. Consideration of the coupling constants and the peak integration values of the observed spectra indicates that a doublet at 21.5ppm is coupled with a triplet at 12.24ppm to give an AX_2 spectrum and two doublets at ~18ppm with two triplets at ~ -8ppm.

The other signals observed in these spectra could be due to a number of different products, among them cyclophosphazenes at higher substitution levels. Consideration of the expected spectra for higher substitution levels, however, reveals that the only material which would yield the observed spectrum is the non-geminal, tetrasubstituted product. Figure (2) in Appendix 1. It is very unlikely that this material would form in preference to the lower levels of substitution and so it can be discounted. Alternative sources of the signals could be rearrangement products. It is known that alkoxyphosphazenes can undergo rearrangement to phosphazanes[58, 61, 194] and although this usually occurs at elevated temperatures (150 - 200°C) it may be catalysed by alkyl halides or HCl to such an extent that the rearrangement has been observed at room temperature[195] (Scheme 3.3.2.). As HCl would be generated during the production of the monosubstituted isopropoxyphosphazene it seems feasible that this rearrangement could occur.

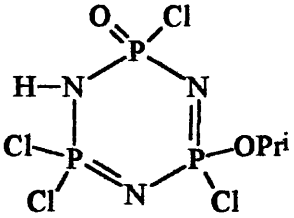
Scheme 3.3.2.



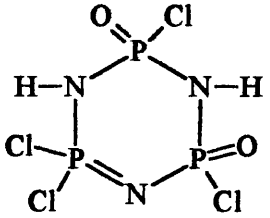
Products which may arise from any rearrangement (and also possibly some further reaction) of the (isopropoxy)phosphazene observed in this study are shown, (XXVII) - (XXIX). Each of these will be discussed in turn.



(XXVII)



(XXVIII)

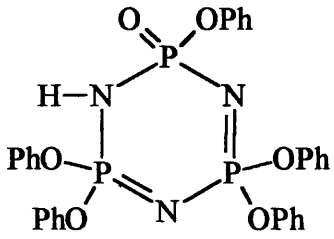


(XXIX)

Compound (XXVII) could be formed from the HCl catalysed rearrangement of a monosubstituted phosphazene and the expected ^{31}P NMR spectrum would depend upon the nitrogen atom to which the proton had migrated. Previous workers have suggested that migration is to an α nitrogen and that the relative basicities of these are important for determining which of these eventually bears the proton[196]. In this case both would be expected to be equally likely.

Exchange between nitrogens has also been observed and the rate of exchange plays a major part in determining the observed ^{31}P NMR spectrum. For example, if exchange is slow then an ABX or AMX spectrum would be expected whereas if it were rapid then it would be expected that the two PCl_2 groups would become equivalent and an AX_2 spectrum would be observed.

This has been shown to be the case for (XXX) in which an AX_2 spectrum is seen at 30°C and an AMX spectrum at -84°C[196]. In addition, similar behaviour has also been observed with the equivalent methoxy derivative.



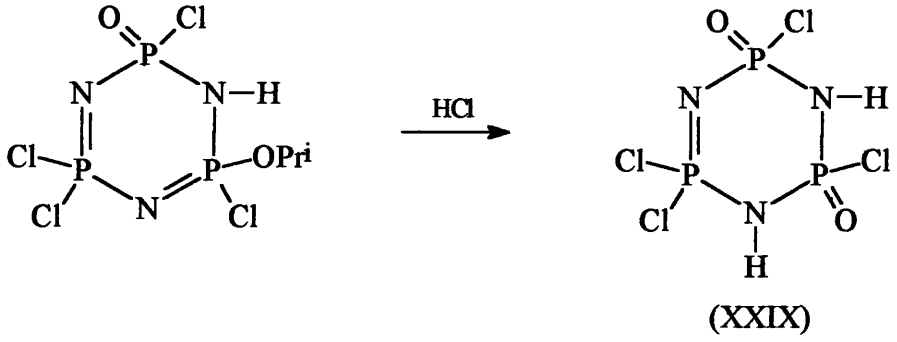
(XXX)

Compound (XXVIII) could be formed from a non-geminally bisubstituted material. Rearrangement is known to occur in stages[15] thus making it possible for this compound to form rather than complete rearrangement of all alkoxy substituents present on the ring. In this case the two α nitrogens are no longer equivalent and it could be expected that one rearrangement product would be more favourable than the other, but with exchange of the proton still occurring.

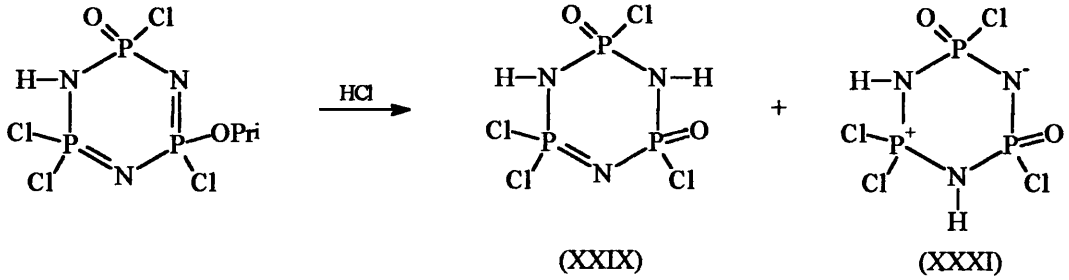
The expected ^{31}P NMR spectrum would consist of two ABX patterns for slow exchange and one for rapid exchange, it would also be expected that one of the two ABX spectra observed for slow exchange would be larger than the other due to one of the rearrangement products being more prevalent than the other. Behaviour which is demonstrated by $N_3HP_3Ph_2(OEt)O$.

Further rearrangement of compound (XXVIII) could result in a number of products depending upon which of the two phosphazadienes is reacting. (Scheme 3.3.5.)

Scheme 3.3.5.



(XXIX)



(XXIX) (XXXI)

As can be seen, (XXIX) is formed in both cases and would be by far the most stable and hence most likely to form. The ^{31}P NMR specrum of this material would be predicted to consist of an ABX type pattern.

The observed spectrum, two doublets and two triplets, would suggest that the patterns could arise from either two AX_2 spectra or to one ABX spectrum in which some signals overlap.

The overlapping ABX spectrum can be discounted when the values of coupling constants are measured from the spectrum.

In (XXIX), J_{AB} =102.6 Hz, J_{AC} = 53.5 Hz and J_{BC} = 53.5 Hz.

(where J_{AB} and J_{AC} were measured from the doublets in the PCl_2 region and J_{BC} from the triplets. - Figure 3.3.3.)

No combinations of these measured coupling constants can be envisaged which would display two triplets and two doublets.

i.e. for P_A - as $J_{AB} > J_{AC}$ a doublet of doublets would be seen.

for P_B - as $J_{AB} > J_{BC}$ a doublet of doublets would be seen.

for P_C - as $J_{AC} = J_{BC}$ a triplet would be seen due to overlap of the two doublets in a doublet of doublets.

On the basis of this data it is evident that this spectrum is not the result of an ABX system, i.e. (XXIX). As compound (XXVIII) would also be expected to display an ABX spectrum, it too, can be discounted.

Compound (XXVII) could result in an AX_2 spectrum and so it is possible that the observed signals are due to this material, however, no explanation as to why two such patterns are observed is immediately obvious from the structure of the material. The answer to this problem may be found when the by-products of the HCl catalysed rearrangement are considered.

During the reaction, 2-chloropropane would be formed and as previously stated, alkyl halides are also known to catalyse the rearrangement of alkoxyphosphazenes. If this was indeed happening then the expected product would be a phosphazadiene with an isopropyl group attached to the nitrogen (XXXII) which would have essentially the same structure as compounds (XXVII) and (XXX), and would hence also give rise to an AX_2 spectrum. (Assuming that rapid exchange between nitrogen atoms also existed in this case.)

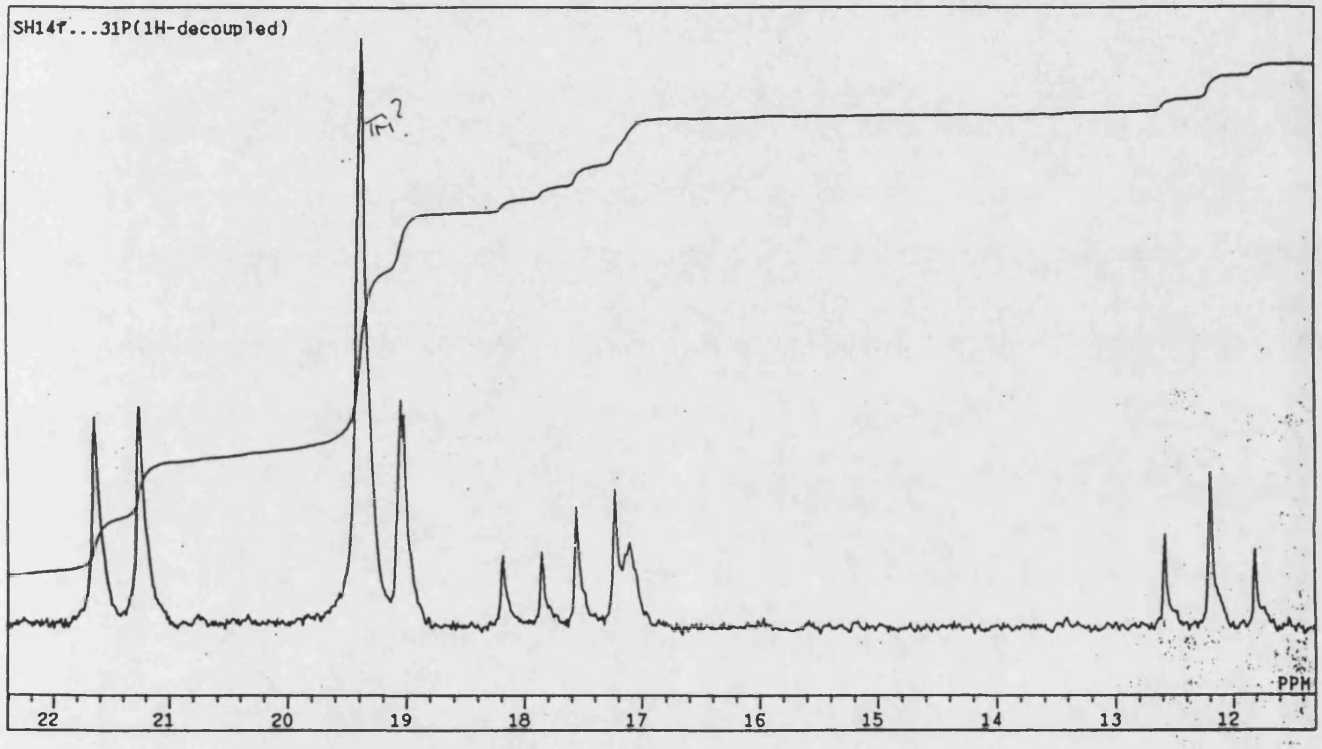
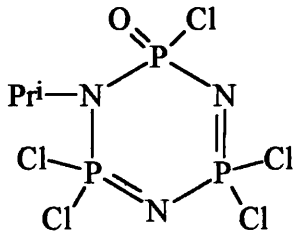


Figure 3.3.3. ^{31}P NMR spectrum from the reaction of PhMgCl with $P_3N_3Cl_6$.



(XXXII)

As it seems likely that the additional signals observed in the spectra are due to reaction of 2-propanol with unreacted $P_3N_3Cl_6$ the relative amounts of these calculated from the ^{31}P NMR spectrum can be added to that of $P_3N_3Cl_6$. This gives an indication of the amount of unreacted $P_3N_3Cl_6$ remaining in its reaction with RMgCl. These are the 'corrected' values given in parentheses in Table 3.3.3 which shows the percentage of observed materials in the reaction with PhMgCl at various times throughout the thermal reaction.

Table 3.3.3: Observed products for the thermal reaction of $P_3N_3Cl_6$ with PhMgCl.

Time (hrs.)	% $P_3N_3Cl_6$ [a]	% $[P_3N_3Cl_4Ph]_2$	% $P_3N_3Cl_5(OC_3H_7)$	% Rearranged products
1	31 (93)	5	62	v. broad, unresolved signals
2	32 (95)	4	49	~14+
3	40 (91)	5	35	~16+
6	30 (92)	7	47	~15+
11	29 (91)	~5 [b]	32	30
20	23 (79)	21	30	27
26	18 (74)	24	31	26

(a) Values in parentheses are the corrected values. Other values are measured directly from the spectrum.

(b) Values preceded by ~ indicate some degree of unresolved peaks in the spectrum and hence a greater uncertainty in the value.

It can be clearly seen, from figure 3.3.4., that as the amount of bi(cyclophosphazene) increases the amount of unreacted $P_3N_3Cl_6$ in the system

decreases. This occurs in the later stages of the reaction more so than in the earlier stages because of the fact that the formation of the bi(cyclophosphazene) is a multi-step process. (Scheme 3.3.1.)

It can also be seen that the amount of monosubstituted isopropoxyphosphazene appears to be greater in the earlier stages of the reaction. It would be expected that as this material arises from the quenching process that the amount present in the system would only depend upon the amount of unreacted trimer available for reaction in the sample. This trend is, effectively observed, however, the sharp fall in the amount of the monosubstituted material in the earlier samples compared with the very gradual decline in the amount of unreacted $P_3N_3Cl_6$ available would seem to oppose this. This may be a phenomenon of the reaction or it may be as a result of the quite considerable scatter observed in the points in this part of the graph i.e. if the percentage of monosubstituted phosphazene at t = 3hrs. was actually higher, then this early slope would be much less severe and the experimental observations would match those predicted much more closely.

If the observations are actually part of the experiment then consideration of the experimental procedure provides an explanation. Samples were removed from the reaction mixture at various times, quenched and prepared for analysis. All samples were then sent for analysis in one batch with the result that those removed first had longer in which to undergo any reaction involving 2-propanol. This is reflected in the greater amount of substitution product observed. The amount of rearrangement products in the system is also observed to follow the same basic trend of the unreacted $P_3N_3Cl_6$, i.e. less products observed as less trimer is available for reaction.

The results from this work concur with previous observations that the organometallic reactions of phosphazenes can be complicated and that various rearrangements of products can add further complications to any studies.

It has been shown that PhMgCl reacts with $P_3N_3Cl_6$ to give only a phenyl substituted bi(cyclophosphazene) product and that ^{t}BuMgCl reacts with $P_3N_3Cl_6$ to give only a monosubstituted alkylphosphazene, this is in agreement with previous work on these systems. It has also been shown that these systems can be complicated by reaction of IPA (added to the reaction system in order to quench the Grignard reactions) with $P_3N_3Cl_6$ and that through further rearrangements, such as the phosphazene to phosphazane rearrangement, that the systems can rapidly become very complex with the result that any attempts to evaluate rates of reaction need to be very careful.

Consideration of the results and available data from these systems led to the decision to study the corresponding ultrasonic reactions as they provided the

possibility for a change in mechanism which could be observed through any change in product distribution relative to the conventional reactions.

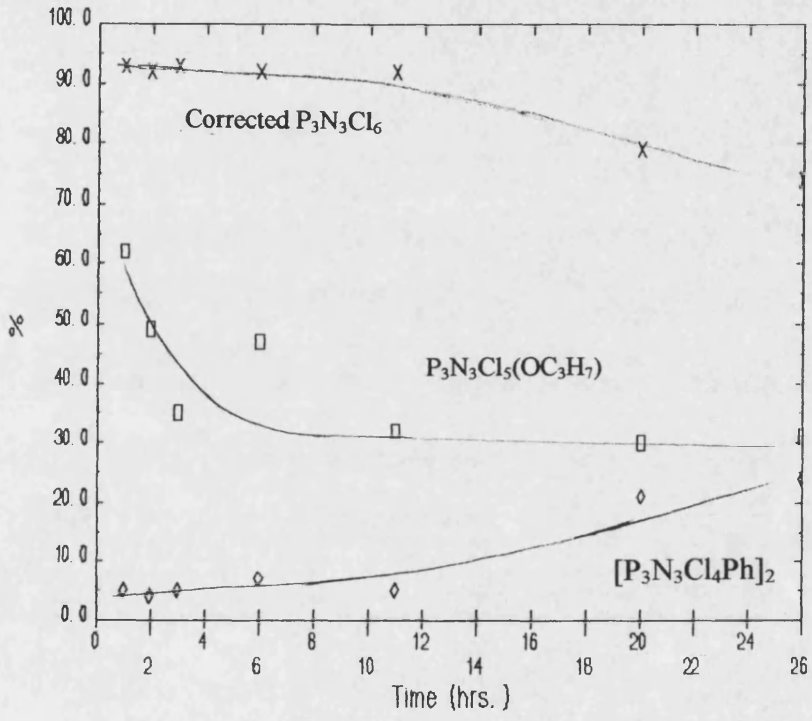


Figure 3.3.4: Graph of the product distribution vs. reaction time for the thermal reaction of $P_3N_3Cl_6$ with PhMgCl.

3.4 REACTION WITH 2,4,6-TRI-t-BUTYLPHENOL

The introduction of strain into a phosphazene ring has been shown to aid the polymerisation procedure in some cases, for example, the transannular bridged species shown in scheme 1.8.3.[99] For this reason, and as a comparison to the smaller p-cresol ligand, it was decided to try to substitute $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol. It was expected that, unlike the p-cresol ligand which yielded approximately equal amounts of cis and trans isomers when non-geminally substituted, the 2,4,6-tri-t-butylphenol ligand would produce only the trans isomer and that a limit to the level to which substitution occurred might be observed. This would be due mainly to the size difference between the two ligands. The 2,4,6-tri-t-butylphenoxy group, being that much larger than the p-cresoxy ligand, would be subject to much greater steric hindrance in a cis isomer than it would in a trans isomer. The same argument applies for the difficult formation of geminally substituted phosphazenes, which would be inevitable at higher levels of substitution.

Initial attempts centred on the same technique as that used in the p-cresol reactions, reaction with the sodium salt of the phenol. However, this proved only to yield a complex mixture with a complicated ^{31}P NMR spectrum. Figure 3.4.1.

The nature of the spectrum was such that many doublet - triplet substitution patterns were observed. Most were difficult to assign, although, 2D COSY NMR aided this process. The only completely unambiguous assignment which could be made was that a large amount of unreacted $P_3N_3Cl_6$ remained in the system and that this varied between 32 and 50%. The most successful separation technique found for this complicated system was fractional crystallisation from warm acetonitrile, however, this only succeeded in separating unreacted $P_3N_3Cl_6$.

For this reason alternative ways of simplifying the system were sought, the first of which was the inclusion of trace amounts of Bu_4NBr in the reaction system in order to aid ionisation of the sodium salt.[197] This resulted in a greater amount of unreacted $P_3N_3Cl_6$ (~80%) being present in the system, however, many of the signals noted in the previous attempts were not observed in the ^{31}P NMR. It would appear that the presence of Bu_4NBr resulted in a simpler reaction process, but, whether this was due to its action aiding the intended reaction or by inhibiting other, side reactions, is unclear. It would certainly seem that little substitution was occurring in these reactions as few of the expected simple substitution patterns were identified.

The reaction of 2,4,6-tri-t-butylphenol, as the unaltered phenol, in the presence of Na_2CO_3 as a hydrogen halide acceptor was also tried. This resulted in a simpler product mixture, as did the presence of Bu_4NBr. However, a complex ^{31}P NMR

spectrum was still observed which had no real consistency between reactions. (Signals were found in similar regions of the spectra, however, patterns which could be observed in one reaction, more often than not, were not observed in another.) Alteration of the reaction stoichiometry and the reaction temperature also did nothing to aid understanding of the system.

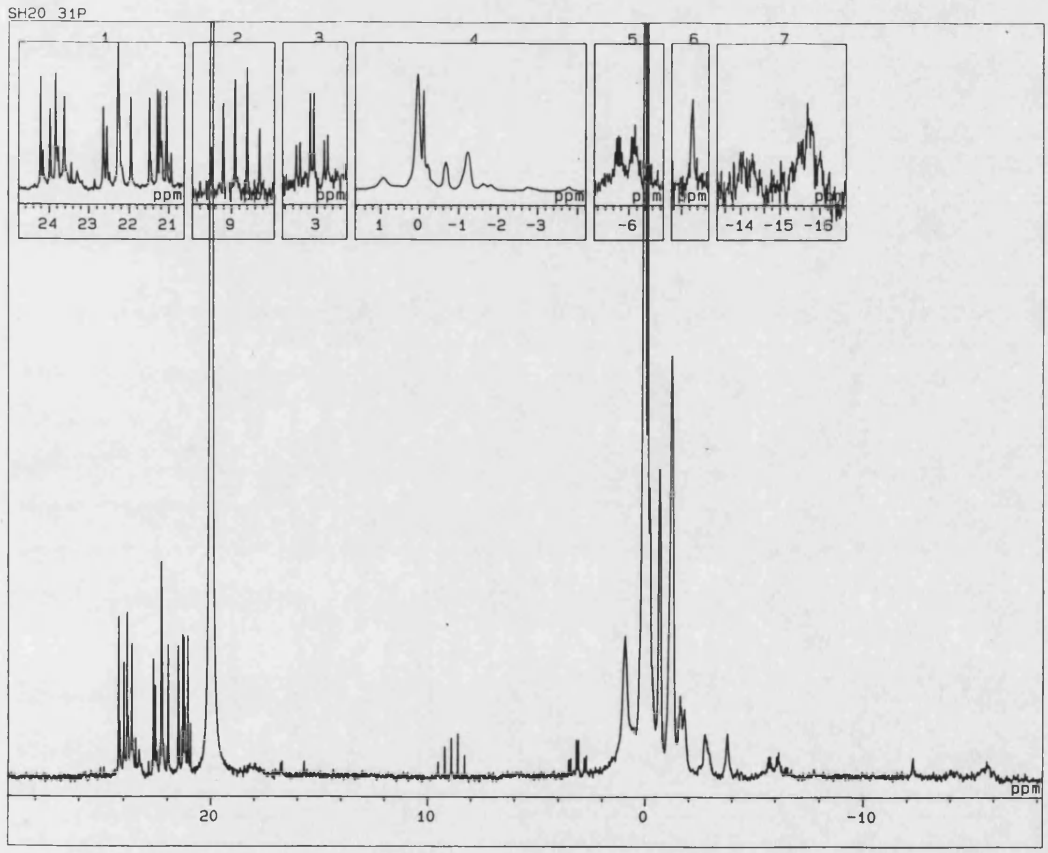
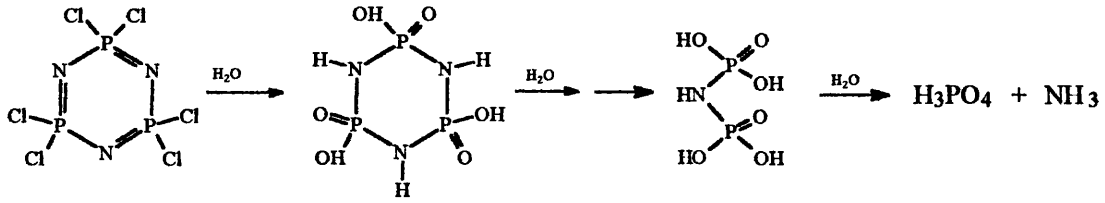


Figure 3.4.1. ^{31}P NMR spectrum of the reaction of sodium tri-t-butylphenoxide with $P_3N_3Cl_6$.

Several possibilities exist for what side reactions may be occurring in the attempted substitution reactions. Phosphazenes are known to be susceptible to hydrolysis and some samples from earlier attempts at substituting 2,4,6-tri-t-butylphenol onto the phosphazene ring were observed to have darkened in colour and were giving off acidic fumes after having been left for a period of several weeks. ^{31}P NMR analysis revealed new signals around the 0ppm region. This suggested that hydrolysis may be occurring to the product mixture as the expected products from hydrolysis of phosphazenes are HCl, phosphoric acid and derivatives of phosphoric acid.

Scheme 3.4.2.



This hydrolysis may have been occurring at the cyclic level or, the introduction of large 2,4,6-tri-t-butylphenol groups may have resulted in ring opening and subsequent hydrolysis. If ring opening was occurring then along with the expected ^{31}P NMR signals from the cyclic products others might also be observed thus complicating the spectrum, this however, is mere speculation as insufficient analytical evidence is available to come to any firm conclusion.

Another possibility arises from recent work by Hökelek *et al*[198] who report the formation of a bi(cyclophosphazene) in conjunction with a mono-substituted phosphazene when the sodium salt of 2,4-di-t-butylphenol is reacted with $P_3N_3Cl_6$. It is also reported that any remaining chlorine atoms could also be replaced by further 2,4-di-t-butylphenoxy groups. No mechanism for the formation of this bi(cyclophosphazene) was mentioned, however, although it might be reasonably expected that a metal - halogen exchange process was occurring as is observed in reactions of $P_3N_3Cl_6$ with Grignard reagents and organocopper reagents.[66b, 78]

It is also known that these bi(cyclophosphazenes) may be cleaved across the P-P bridging bond by nucleophiles[199] such as alkoxy and aryloxy groups. Again this could give rise to a complicated ^{31}P NMR spectrum.

Table 3.4.1 shows the more consistent ^{31}P NMR data which could be extracted from the various reactions of 2,4,6-tri-t-butylphenol with $P_3N_3Cl_6$.

Table 3.4.1. ^{31}P NMR data extracted from the reactions of $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol

Compound	Chemical shift (ppm)			
	δPCl_2	$\delta PCl(OR)$	$\delta P(P)R$	$^2J_{PP}$ (Hz.)
unreacted $P_3N_3Cl_6$	19.6			
$P_3N_3Cl_5[OC_6H_2(C_4H_9)_3]$	22.5 (d)	3.0 (t)		61.4 - 65.4
$[P_3N_3Cl_4[OC_6H_2(C_4H_9)_3]]_2$[a]	22.0 (m)		9.0 (m)	63.5

(a) only observed in reactions with the sodium salt of 2,4,6-tri-t-butylphenol.

These assignments are based upon coupling constants and integration observed in the spectra and upon NMR assignments in similar compounds.[66b, 199, 200]

The formation of what appears to be the bi(cyclophosphazene) is further suspected from the observation that the signals assigned to this material in the ^{31}P NMR spectrum only appear in the reactions with the sodium salt of 2,4,6-tri-t-butylphenol. If the formation of this product was through a metal - halogen exchange mechanism, as expected, then it would not be expected to be present in the reactions with unaltered phenol in the presence of Na_2CO_3.

The signals assigned to the mono-substituted tri-t-butylphenoxyphosphazene appear in the spectra of all of the experiments carried out and indicate that this material is present in varying amounts which range from ~ 2% to ~ 50% again displaying the irreproducibility of this system.

Following the previously unsuccessful attempts to substitute $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol it was thought that an increase in the polarity of the reaction solvent might facilitate ionisation of the ligand and hence aid substitution. The solvent chosen was DMF as this is more polar than the previously used THF and has successfully been used as a reaction solvent by Shaw and Carroll.[201] for alkylthiolysis of $P_3N_3Cl_6$.

The results of using DMF as a solvent for the reaction were unexpected. Initially the reaction temperature chosen was reflux (153°C), however this proved to result in only a black, insoluble material so a lower temperature (80°C) was chosen for further reactions. The reaction observations are shown in Table 3.4.2.

Table 3.4.2. Observations from the reaction of $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol in differenet solvents.

Solvent	Observations
THF	The reaction proceeded as an orange solution with a Na_2CO_3 suspension. The product obtained was an orange organic soluble solid. The product had a complex ^{31}P NMR spectrum with a chemical shift range of approximately 25 - 0ppm thus indicating that some substitution must be occurring. The predominant feature of the NMR spectrum was unreacted $P_3N_3Cl_6$.
DMF	The reaction proceeded as an orange solution with a Na_2CO_3 suspension, but, also gradually developed an increasing amount of an insoluble material. An orange, organic soluble solid was collected which was found (by ^{31}P NMR) to contain NO phosphorus. Filtration of the crude reaction mixture yielded a white, water soluble solid which had a complex ^{31}P NMR spectrum with a chemical shift range from 5 to -25ppm. The ^{31}P NMR spectrum showed no unreacted $P_3N_3Cl_6$.

It was suspected, from these observations, that the $P_3N_3Cl_6$ in the reaction system was reacting with the DMF solvent. Indeed it appeared that this was occurring to the exclusion of any reaction with 2,4,6-tri-t-butylphenol. The ^{13}C and ^{1}H NMR spectra of the isolated orange solid confirmed that it was unreacted 2,4,6-tri-t-butylphenol.

Further investigation of the conditions under which DMF had been used as a successful reaction solvent by Carroll and Shaw revealed that this was only so below 110°C, above that temperature complete decomposition of the cyclophosphazenes was reported. This decomposition was believed to be caused by an interaction between the DMF and the $P_3N_3Cl_6$. As the reaction with 2,4,6-tri-t-butylphenol had been carried out at 80°C the observed participation of the solvent was unexpected.

The ^{31}P NMR spectrum of the water soluble solid filtered from the reaction mixture consisted of a large number of peaks, many of which were broad, in the 5 to -25ppm range. The complexity of the spectrum was such that no recognisable substitution patterns were apparent and the identification of a specific structure was very difficult, if not impossible.

In order to confirm that $P_3N_3Cl_6$ was reacting with the DMF solvent and to investigate any limitations of any reaction which was occurring, $P_3N_3Cl_6$ was stirred in excess DMF under various conditions. Initially conditions were chosen to match as closely as possible those used in the attempted 2,4,6-tri-t-butylphenol substitution and as such the only difference to that reaction was that the phenol itself was not present.

Again, an organic insoluble solid was formed during the reaction , which, as in the attempted substitution reaction, had a complex ^{31}P NMR spectrum in the 5 to -20ppm chemical shift range. Figure 3.4.2. Because of the broadness of many of the signals no substitution patterns could be identified, although the spectrum was noted to have several features in common with that from the substitution reaction. Again, no unreacted $P_3N_3Cl_6$ was detected.

Peaks at approximately 168ppm in the ^{13}C NMR spectrum, coupled with an IR absorbance at $1650cm^{-1}$ (C=O stretch) would seem to imply an amide group in the product and an IR absorbance at $1240cm^{-1}$ implies the retention of a phosphazene unit. (P-N-P asymmetric stretch).

A reaction was also carried out under the same conditions, but, with no Na_2CO_3 present. The insoluble material was again obtained, however, this time the ^{31}P NMR spectrum was much simpler. Figure 3.4.3. Again, the chemical shift range was in the 0 - -25ppm area and again no definite structural assignments could be made from the spectrum due to the complexity and broadness of the signals masking any patterns which may have been present. Evidence for the existence of an amide group within the product was again provided by the ^{13}C NMR spectrum and the IR spectrum, as was evidence for the presence of a phosphazene unit.

A reaction carried out at 25°C with no Na_2CO_3 present yielded essentially the same analytical information as the reaction carried out at 80°C, it would seem therefore, that although Na_2CO_3 is not essential for any reaction between DMF and $P_3N_3Cl_6$ to occur it is certainly adding to the complexity of the system and very possibly taking part in some side reactions.

When the reactions of both DMF and phosphazenes are considered it is found that both amides and the phosphazene ring are electrophiles, and as such, straight substitution onto the ring would not be expected. Similarly, attack by the amide nitrogen onto the phosphazene ring would also be unexpected due to the formation of a positive charge which has no apparent method of stabilisation.

If an endocyclic phosphazene nitrogen could act as a nucleophile and attack the amide then the reaction shown in scheme 3.4.2 might be expected.

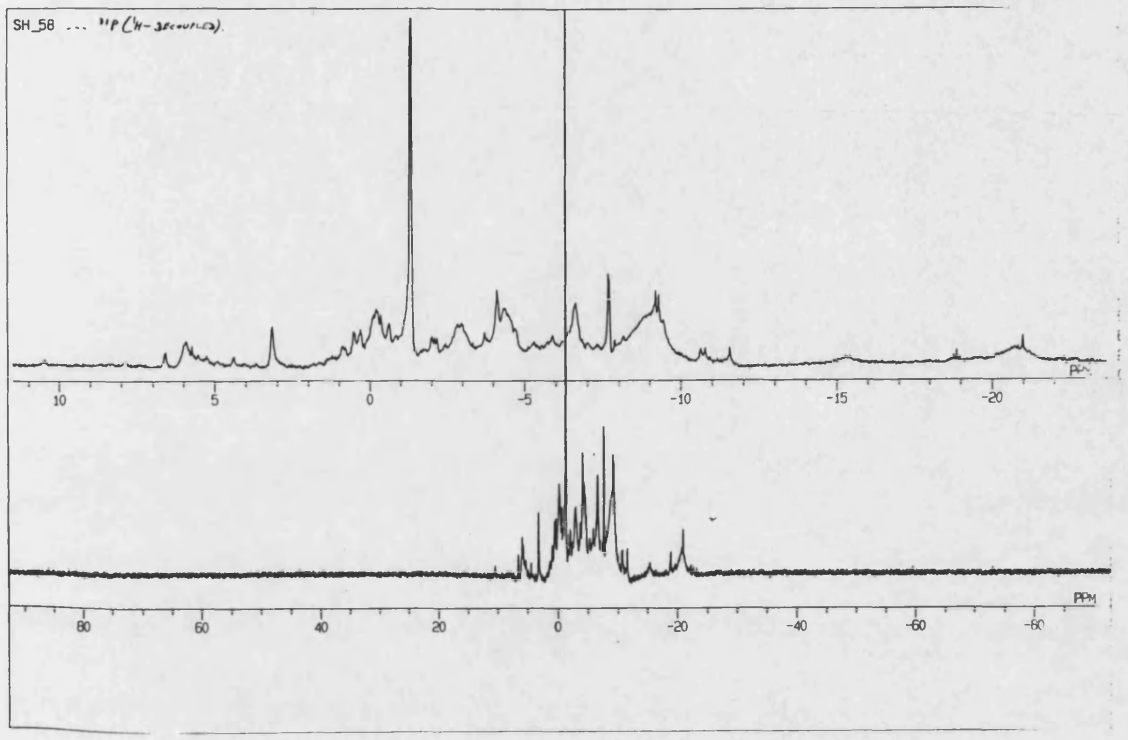


Figure 3.4.2 : ^{31}P NMR of product obtained in reaction of $P_3N_3Cl_6$ with DMF in presence of Na_2CO_3

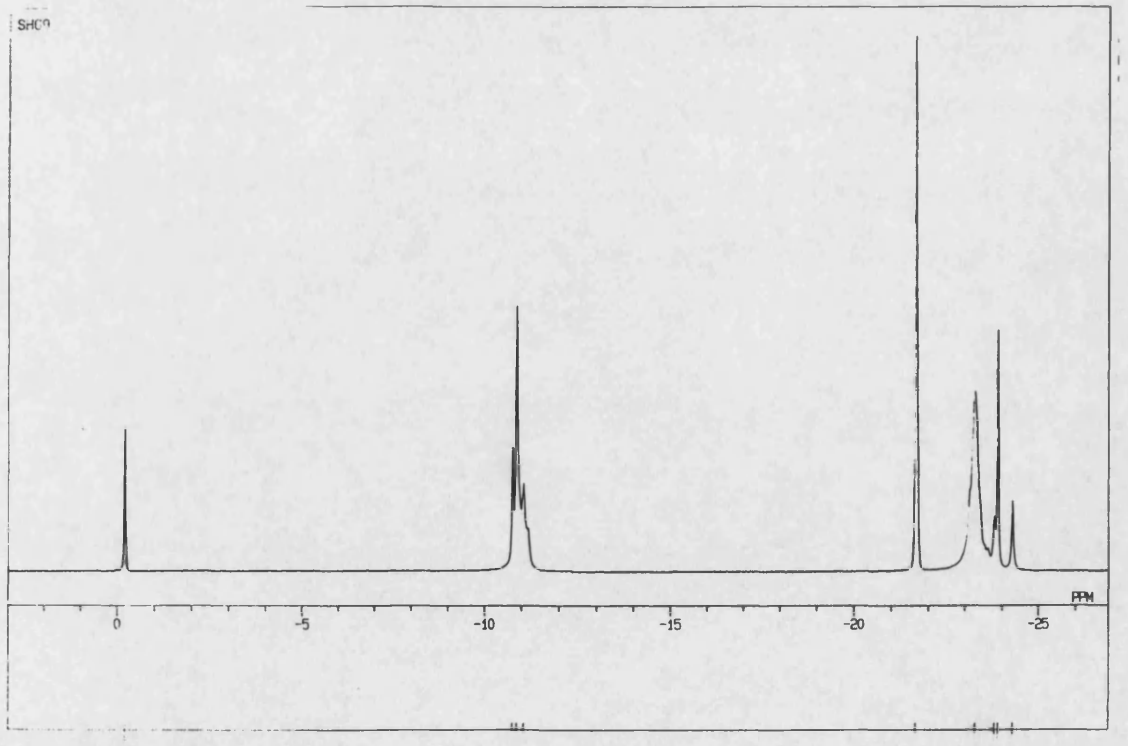
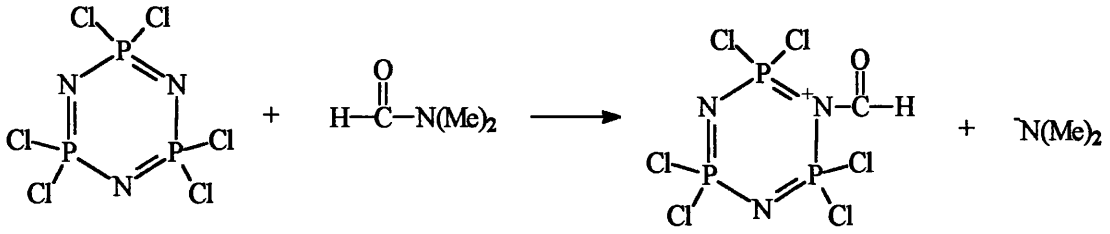


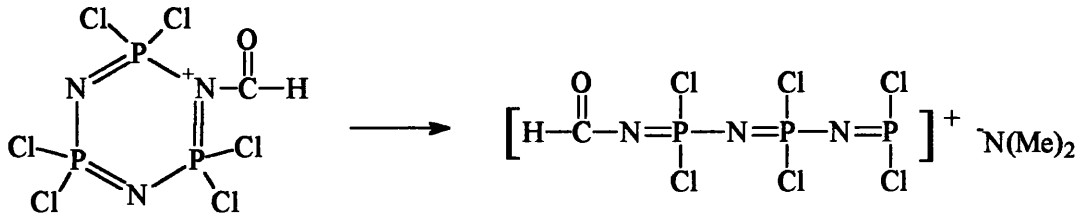
Figure 3.4.3 : ^{31}P NMR of obtained products from reaction of $P_3N_3Cl_6$ with DMF

Scheme 3.4.2.



This leaves a positive charge on the phosphazene, however, if at this stage ring cleavage occurred this could be alleviated.

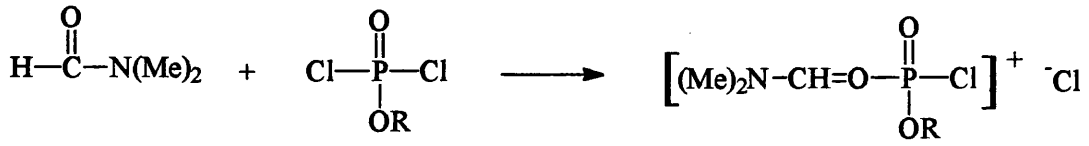
Scheme 3.4.3.



This would result in the retention of an amide function and of phosphazene units and may also explain the fact that none of the usual substitution patterns were observed in the ^{31}P NMR spectrum.

Several reactions are known in which the oxygen atom of an amide is the site of attack and indeed O-protonated amides are known to be resonance stabilised. Shaw and Carroll[201] suggested that DMF reacts with phosphazene P-Cl bonds in a similar way to that in which it forms adducts with phosphorus oxychloride and its alkoxy derivatives.[202] Scheme 3.4.4.

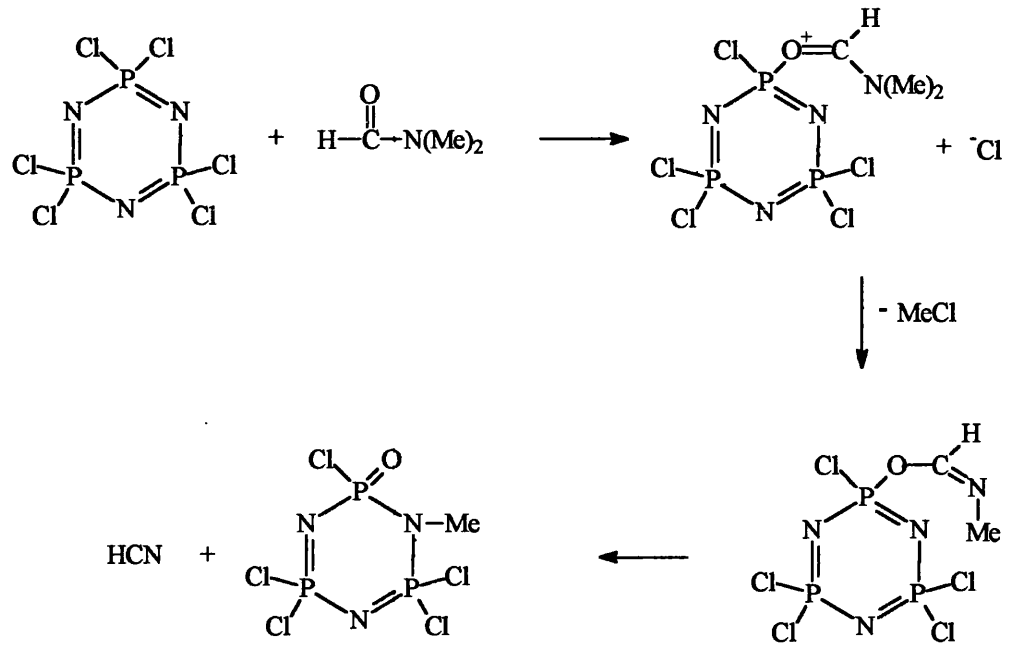
Scheme 3.4.4.



Graham and Marr[203] extended this idea to suggest a mechanism for the rapid dehydration of some amides by $P_3N_3Cl_6$ to give nitriles, however, the mechanism proposed in their work appears to require protons on the amide nitrogen for it to proceed.

If this mechanism were to be applied to the reaction with DMF then it might be expected to yield a cyclic N-methyl substituted phosphazene, HCN and MeCl.

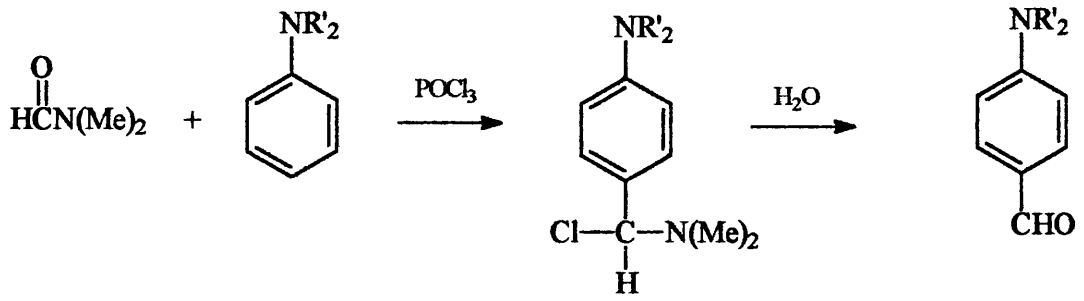
Scheme 3.4.5.



No evidence of HCN or MeCl was detected in any of the analytical data nor, indeed in any repeated reaction observations and, as DMF was in excess in the reaction system, it might reasonably be expected that a more fully substituted product would be obtained, possibly leading to a cyclophosphazane with no phosphazene units remaining in the ring. This is clearly also contradicting the IR evidence. Even if a partially substituted ring product, which did contain phosphazene units, were to be obtained, then the observed ^{31}P NMR spectra do not conform with the product structure. As in the Grignard reaction systems (Section 3.3) either an AX_2 or an AXX' spectrum might be expected.

An extension of the adduct forming idea is based upon the Vilsmeier reaction[204] (the reaction of an aromatic amine with DMF and phosphorus oxychloride to form aldehydes).

Scheme 3.4.6.



If this could be extended and applied to a phosphazene system it could be envisaged that a phosphazene ring bearing a C(O)H group on an endocyclic nitrogen atom may be obtained. Scheme 3.4.7.

Again, this could be occurring at more than one site around the phosphazene ring resulting in a cyclophosphazane and the same problem encountered with Graham and Marr's mechanism, i.e. the loss of the phosphazene units. However, this possible reaction route has in its favour the retention of an amide function.

Of all of the possibilities suggested, none appear to provide a conclusive solution to the question of how DMF reacts with $P_3N_3Cl_6$, however, based upon the available analytical information it seems most likely that the reaction with a phosphazene endocyclic nitrogen atom provides the closest answer, albeit with problems. It is also suggested that some reaction with the amide oxygen is occurring in conjunction with other reactions thus complicating the system and resulting in a complex mixture of products.

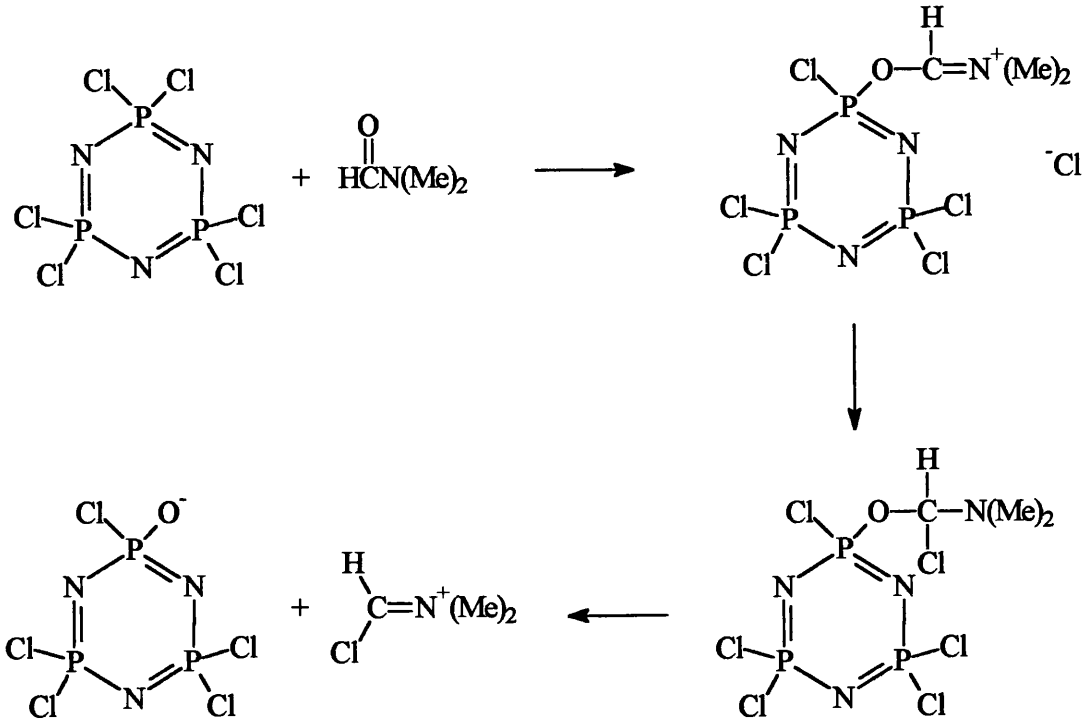
The NMR spectra would certainly suggest a mixture of products, especially when Na_2CO_3 is present in the system, although all attempts which were made to separate any such mixture failed. These attempts included various chromatographic methods (including GPC).

The more complex nature of the reaction system when Na_2CO_3 was present could indicate that the Vilsmeier type reaction was occurring. HCl would be an expected by-product from this process and Na_2CO_3 was initially present in the reaction mixture as a hydrogen halide acceptor. It may well be that when no Na_2CO_3 is present this Vilsmeier type reaction has less of a driving force and so a simpler system is obtained. It can also be seen that without the presence of water then the reaction would not proceed to completion, as a result a vigorous drying procedure was sought for DMF.[205]

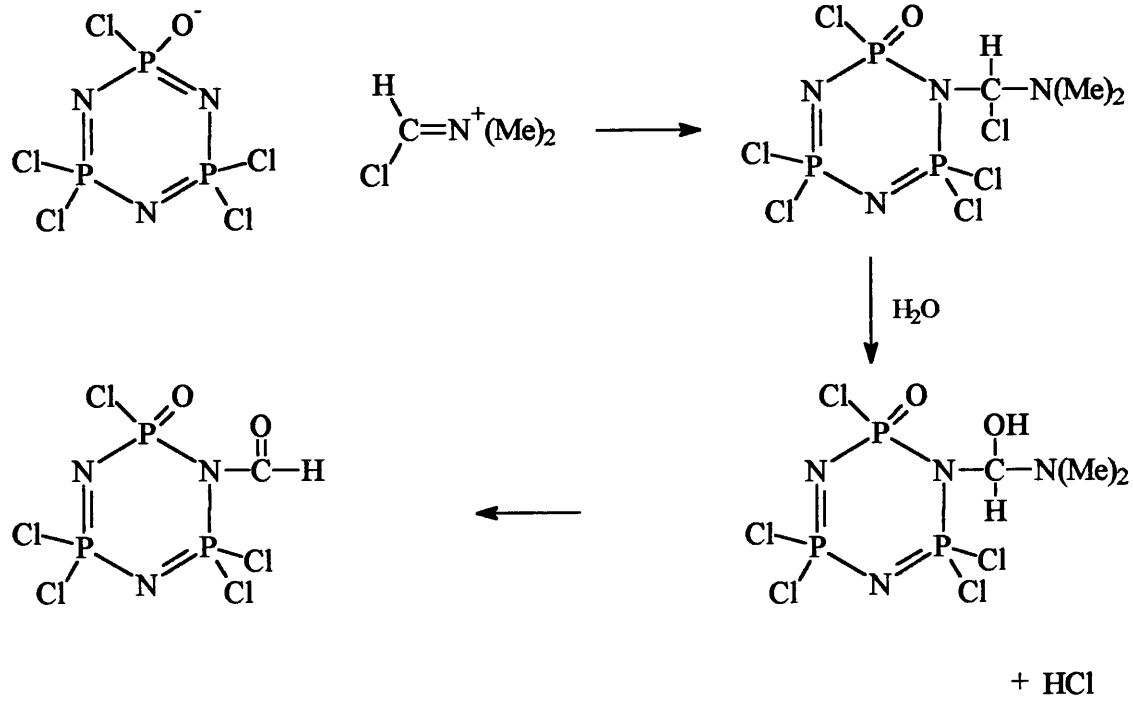
Following azeotropic distillation with benzene (in a ratio of 10:1 DMF:benzene) the residual solvent was shaken with activated alumina, filtered and

then distilled under reduced pressure. The fraction distilling at 40°C \ 10mm Hg was collected and was used in a further reaction of DMF with $P_3N_3Cl_6$ at 25°C. In this case no reaction was observed, ^{31}P NMR showed only unreacted $P_3N_3Cl_6$ thus indicating that the presence of H_2O must indeed be required for the reaction of $P_3N_3Cl_6$ with DMF to procede.

Scheme 3.4.7.



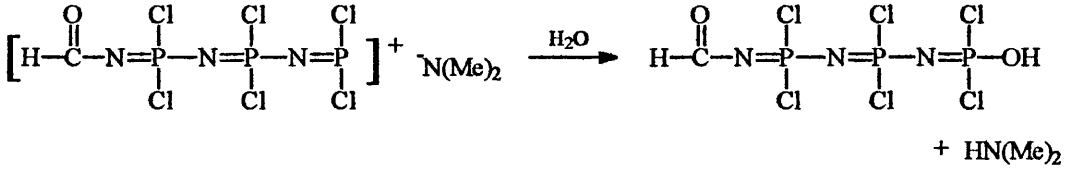
then,



+ HCl

The reaction of an endocyclic phosphazene nitrogen atom with DMF does not appear to require the presence of water, so it could be expected that some reaction should still have occurred with the dried DMF. It may be, however, that water stabilises the ring opened product and is thus needed for the reaction to occur. Scheme 3.4.8.

Scheme 3.4.8.



If this was the case then dimethylamine should be detectable among the final products. Inspection of the spectra reveal signals in the correct chemical shift range (dimethylamine would be expected to have signals at $\delta C_{(Me)}$ = 35.4ppm, $\delta H_{(Me)}$ = 1.90ppm and $\delta H_{(H\text{-}N)}$ = 0.5 - 4.5ppm). Figure 3.4.4. This indicates that this process could indeed be taking place.

The use of the rigorously dried DMF as a solvent in the reaction of $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol was tried, with more encouraging results. Rather than the previously obtained, complex ^{31}P NMR, on this occasion a much simpler spectrum was observed, figure 3.4.5., however, none of the signals present (with the exception of the unreacted $P_3N_3Cl_6$ peak) were observed in the previous substitution attempts in THF solvent. Another complication was that of the irreproducibility of the reaction, all of the ^{31}P NMR spectra were different save for the $P_3N_3Cl_6$ peak and more work is needed in this area in order to elucidate what is occurring.

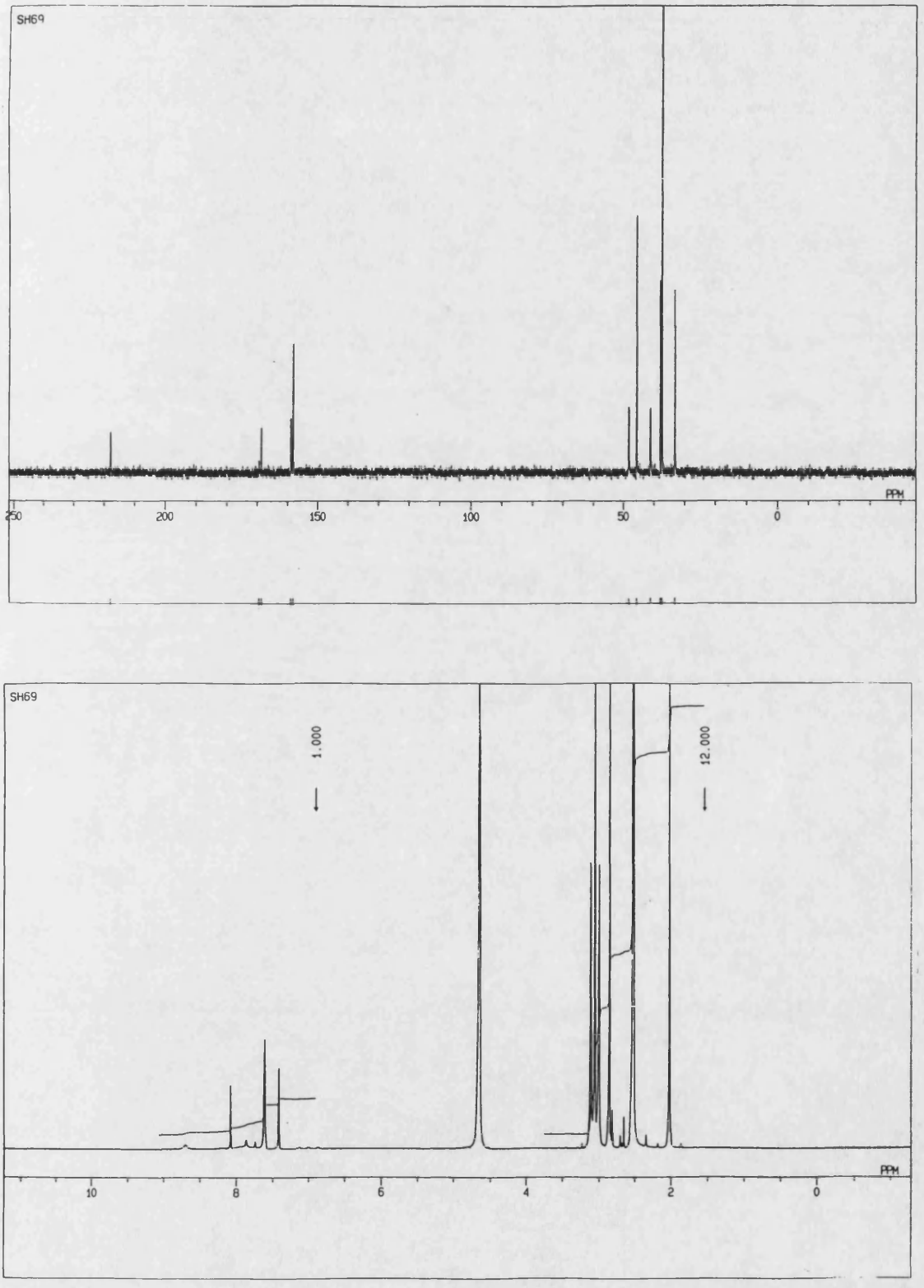


Figure 3.4.4. ^{13}C and ^{1}H NMR spectra of the reaction products in the reaction of $P_3N_3Cl_6$ with DMF

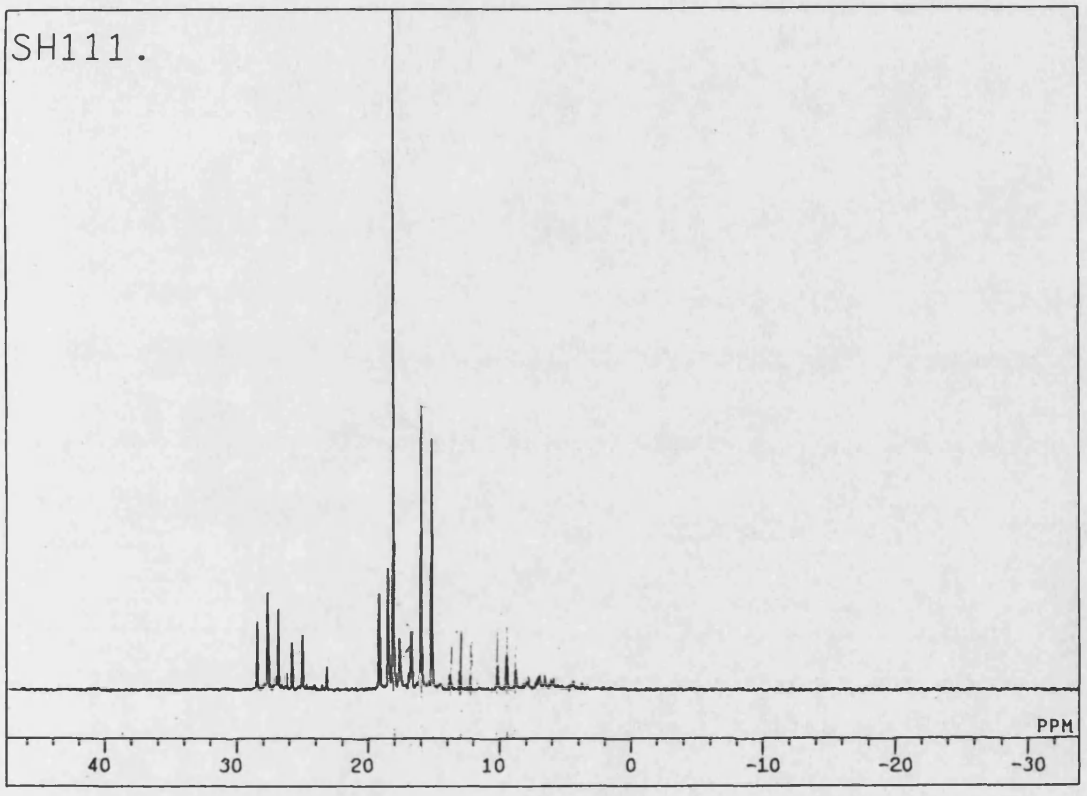


Figure 3.4.5. ^{31}P NMR spectrum of the reaction products in the reaction of $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol in rigorously dried DMF.

Although several ideas have been put forward here to explain what is occurring in the reaction between DMF and $P_3N_3Cl_6$ none of them has been conclusively proven, it is suggested that the most likely scenario, based upon the data available, is that several reactions are taking place simultaneously. This seems especially so in the presence of Na_2CO_3. The result is the formation of a complex mixture of products consisting of some of the expected monosubstituted phosphazene and some bi(cyclophosphazene). Attempts to try to identify some of the other products formed and to try to simplify the system led to the identification of some possible products from the reaction of $P_3N_3Cl_6$ with DMF in which several routes appear to be possible. These include a phosphazane obtained from a reaction similar in nature to the Vilsmeier reaction between an aromatic amine and DMF and a linear phosphazene species obtained from reaction of an endocyclic phosphazene nitrogen atom with DMF followed by ring cleavage.

In view of the irreproducibility which was observed in this system, in terms of the ^{31}P NMR spectra and the amounts of products present which could be identified from the very complex spectra, it was decided not to continue studies of this ligand at either the polymeric level or in ultrasonic reactions.

3.5 REACTION WITH GLYCIDOL, [(HYDROXYMETHYL)OXIRANE.]

In order to be able to introduce even more control into the properties of a particular polyphosphazene it would be advantageous to be able to alter any side groups present on that polymer to others which may provide properties more suited for the purpose at hand. This could be made possible if a single polymer could be synthesised which bore side groups that could undergo further reaction to yield one or more different types of side group.[206]

An example of such a material would be a polyphosphazene bearing glycidyl side groups, obtained from the reaction of glycidol with polydichlorophosphazene. Cleavage of the epoxide ring present in this substituent would provide a route to a glycol side group which could then be reacted even further to yield a wide variety of different functional groups and hence properties.

Before advancing to the stage of attempting to substitute polydichlorophosphazene, however, it was decided to study the reaction of the trimeric chlorophosphazene in order to try to deduce the most suitable conditions for the polymer substitution.

Initial attempts centred on the same method which had proved successful with the p-cresol system, that of the reaction of the sodium salt of glycidol with $P_3N_3Cl_6$.

Results were disappointing as the substitution proved to be completely unsuccessful. ^{31}P NMR showed only unreacted $P_3N_3Cl_6$ present in the system and 95%+ of that used in the reaction was recovered following the work up procedure.

Glycidol is known to auto-polymerise at slightly elevated temperatures and so it was thought that this may be occurring rather than reaction with sodium and / or substitution of the phosphazene. This idea was tested with analysis of a sample from the reaction of sodium with glycidol and it was found that polymerisation, to some extent at least, was indeed occurring. It was also noted that a sample of glycidol straight from the bottle also contained a significant amount of impurities, however, even though distillation at reduced pressures removed these impurities still no substitution of the phosphazene was observed. The ^{1}H and ^{13}C NMR data for these reactions is given in Table 3.5.1.

Following these unsuccessful attempts a method was sought which would reduce,or ideally eliminate, the polymerisation of glycidol. The reaction of glycidol directly with the phosphazene in the presence of a hydrogen halide acceptor, such as Na_2CO_3, would be a one step reaction, rather than two as in the reaction with the sodium salt, and so should accomplish this.

The use of this method resulted in the observation of some substitution, however, the ^{31}P, ^{1}H and ^{13}C NMR spectra for the various reactions performed were very complex and indicated that other reactions were taking place in conjunction with the expected substitution reaction and substantial parts of the observed ^{31}P NMR spectra were noted to consist of the doublet - triplet patterns associated with a substituted phosphazene ring.

Various experiments were carried out (such as altering the reaction stoichiometry and temperature) in order to try to elucidate what products were being formed during the reaction. However, as in the reactions with 2,4,6-tri-t-butylphenol, results were inconsistent and only a limited number of the NMR signals were observed in spectra from throughout the various experiments carried out. These are listed in table 3.5.2. The large number of additional, more inconsistent signals observed in the various ^{31}P NMR spectra (generally in the 0 ppm to 10 ppm and the 20 to 30 ppm range) are not listed here. The amounts of the products which could be given a possible assignment were also observed to vary throughout the experiments although no correlation to any experimental parameter could be found.

Table 3.5.1.

Material	^{1}H data	^{13}C data
Distilled glycidol	epoxide $-CH_2-$ 2.81ppm (d of d), J=4.21Hz, 2.70ppm (d of d), J=2.75Hz, J'=4.94Hz epoxide -CH 3.15ppm (m) $-CH_2-O-$ 3.89ppm (d of d), J=2.56Hz. 3.53ppm (d of d), J=5.13Hz. J'=12.64Hz. -OH 3.87ppm	61.80ppm epoxide CH 52.06ppm $-CH_2-O-$ 43.90ppm epoxide CH_2
Glycidol from bottle	epoxide $-CH_2$ 2.82ppm (m), J=4.76Hz. 2.73ppm (d of d), J=2.8Hz. J'=4.86Hz. epoxide -CH 3.164ppm (m) $-CH_2-O-$ 3.9 - 4.0ppm (m) 3.6ppm (m), both broad signals with no clear splitting patterns -OH 2.996ppm other signals 3.4 - 3.5ppm 3.6 - 3.7ppm, both broad multiplets with no clear splitting patterns 1.2ppm (m)	61.93ppm epoxide CH 52.30ppm $-CH_2-O-$ 44.18ppm epoxide CH_2 others 63.49ppm 57.88ppm 17.94ppm

Table 3.5.1 (continued)

Sodium + glycidol	epoxide -CH_2 2.7ppm (m) 2.8ppm (m), both broad signals with no clear splitting patterns epoxide -CH 3.19ppm (m) -CH_2-O- 3.5 - 4.0ppm, broad, complex region with no clear splitting patterns. -OH 2.25ppm others 1.86ppm (m) 1.25ppm (s)	

(d of d) = doublet of doublets, (m) = multiplet, J = coupling between the signals in the doublets, J' = coupling between the doublets.

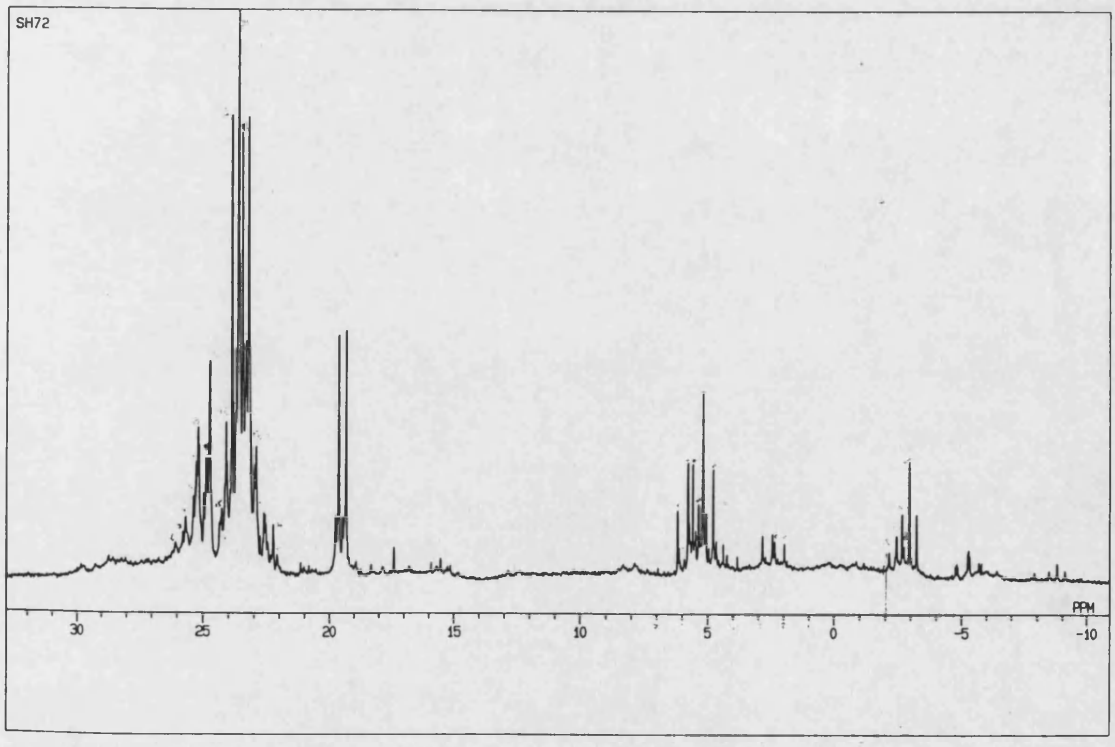


Figure 3.5.1. example of complexity of ^{31}P spectra.

Table 3.5.2.

^{31}P NMR signals[a]	^{1}H NMR signals[a]	^{13}C NMR signals[a]
22 - 22.5ppm (d) 14.5 - 15.5ppm (t) J = 61.4 - 63.4 Hz	signals associated with unreacted glycidol (see table 3.5.1)	traces of unreacted glycidol (see table 3.5.1.)
		71.61ppm
23.7ppm (m) generally d 5.4ppm (m) generally t J = 63.4 - 67.4 Hz. [b]	4.36ppm (t) [b] 4.05 - 4.1ppm (m) broad 3.88ppm (d) 3.75ppm (m)	70.56ppm 67.85ppm [b] 63.38ppm 50.81ppm
19.5ppm (d) -2 - 0ppm (t) J = 63.4 - 65.5 Hz	3.67ppm (d) 2.27ppm (m) 2.17ppm (m) broad [b]	44.76ppm 44.08ppm 25.45ppm [b]
17.5ppm (s) [b]		

s = singlet, d = doublet, t = triplet and m = multiplet

(a) The various NMR signals in the above table are assigned in the following text.

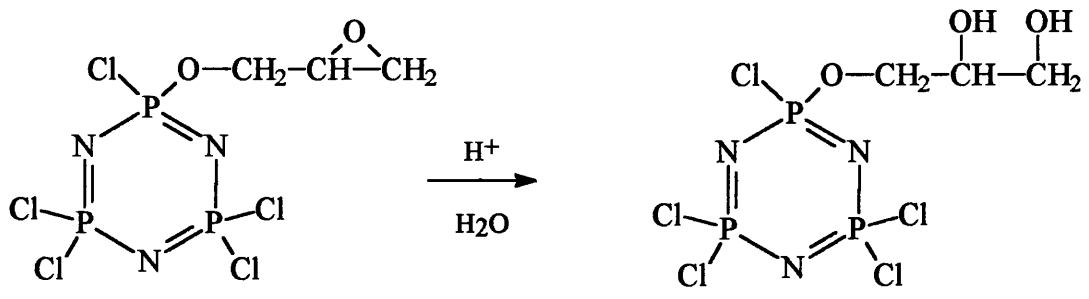
(b) these signals were only observed in 1:6 stoichiometric reactions.

Consideration of the various side reactions which would be taking place reveal a number of possibilities which could be occurring either individually or collectively.

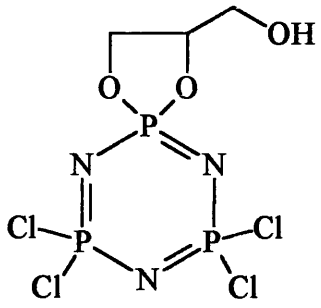
Two possibilities exist for the further reaction of the glycidol epoxide ring, hydrolysis and nucleophilic substitution.

If hydrolysis, the ring would be expected to open to yield a glycol unit and any further reaction would be reasonably expected to give products similar to those obtained from the reaction of $P_3N_3Cl_6$ with glycerol. Scheme 3.5.1.

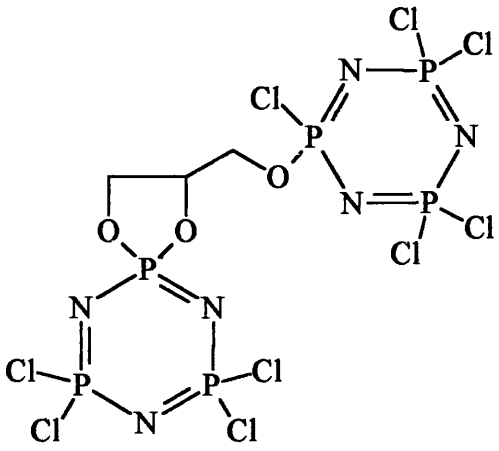
Scheme3.5.1.



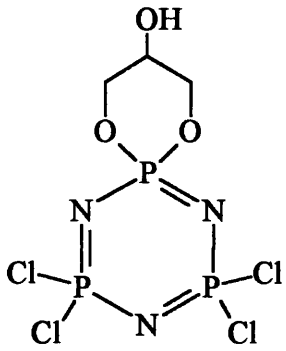
Studies carried out by Shaw and his co-workers[207] suggest that there are four possible reaction products when glycerol reacts with $P_3N_3Cl_6$. (XXXIII) - (XXXVI)



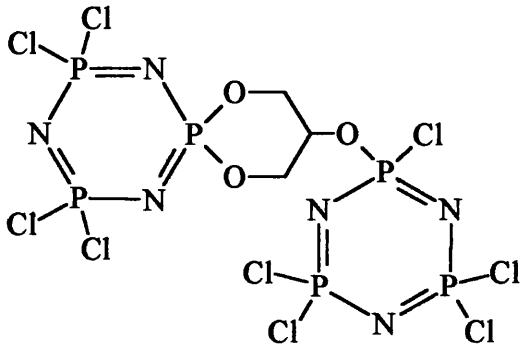
(XXXIII)



(XXXIV)



(XXXV)



(XXXVI)

Comparisons with work performed to deduce the relationship between OPO bond angles in cyclic phosphate esters and their chemical shifts[208] revealed that (XXXIII) and (XXXIV) were the major products from the reaction. Tables 3.5.3 and 3.5.4.

Table 3.5.3. ^{31}P NMR data for products obtained in the reaction of glycerol with $P_3N_3Cl_6$[207]

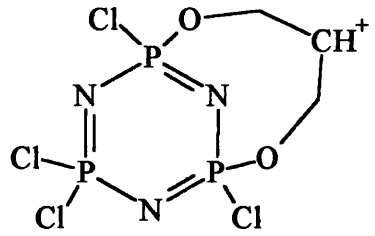
Compound	$\delta P_{(spiro)}$	δPCl_2	$\delta PCl(OR)$	$^2J_{PP}$ (Hz)
(XXXIII)	24.7ppm	26.2ppm		64.7
(XXXIV)	24.2ppm	26.3ppm 23.5ppm	16.8ppm	66.1 Hz 65.2 Hz

Table 3.5.4 Relation between OPO bond angles in cyclic phosphate esters and associated chemical shifts.[208]

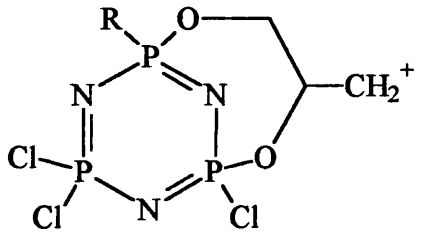
Ring size	OPO ∠	$\delta P_{(spiro)}$	δPCl_2	$^2J_{PP}$ (Hz)
5 - membered	98.3°	23.8ppm	25.5ppm	67.0
6 - membered	105.4°	2.4ppm	23.3ppm	69.2
7 - membered	106.1°	9.2ppm	22.8ppm	71.0

The alternative ring opening route, nucleophilic attack of the epoxide ring oxygen on a phosphazene phosphorus atom, could result in a number of products. (XXXVII) - (XLI).

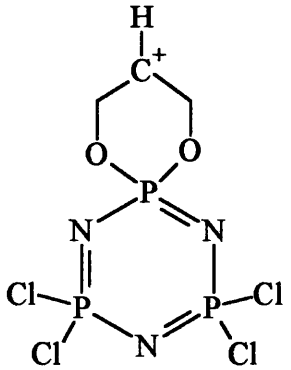
Due to inductive effects, species (XXXVII), (XXXIX) and (XLI) would be expected to be the most stable. These could be considered to be equivalent / similar to the products obtained when 1,3-propanediol reacts with $P_3N_3Cl_6$. (XLII) - (XLV)



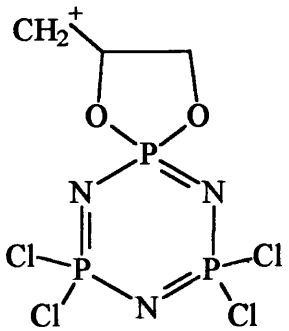
(XXXVII)



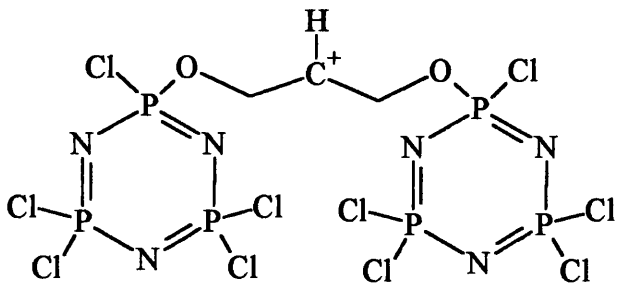
(XXXVIII)



(XXXIX)



(XL)

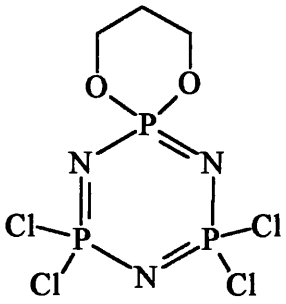


(XLI)

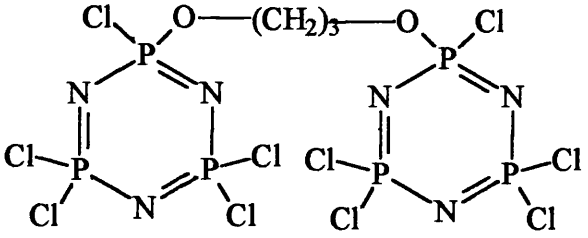
Shaw *et al*[209] found that products were formed as (XLII).> (XLIII)> (XLIV) >> (XLV), and the ^{31}P NMR data for these materials is shown in table 3.5.5.

Table 3.5.5. ^{31}P NMR data from the reaction of 1,3-propanediol with $P_3N_3Cl_6$.[209]

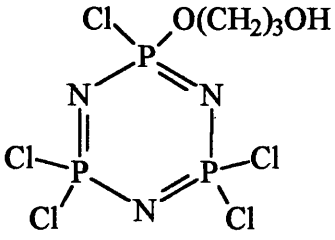
Compound	δPCl_2	$\delta P_{(spiro)}$	$\delta PCl(OR)$
(XLII)	24.1ppm	3.4ppm	
(XLIII)	23.4ppm		16.0ppm
(XLIV)	23.5ppm		16.1ppm
(XLV)	29.5ppm		30.05ppm



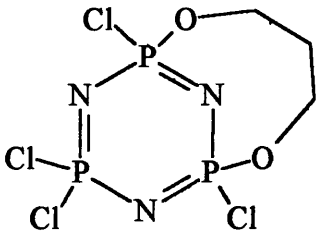
(XLII)



(XLIII)



(XLIV)



(XLV)

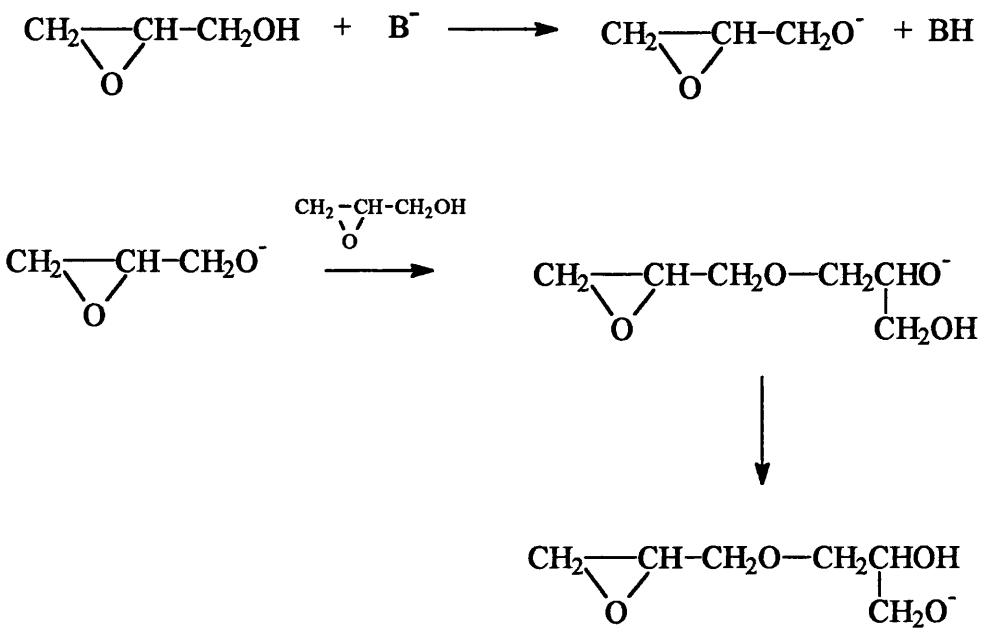
As an expected side product of the initial substitution reaction would be HCl the hydrolysis route seems likely. However, all of the reagents in the reaction were dried prior to use and, coupled with the presence of Na_2CO_3, acting as a hydrogen halide acceptor, it would apear that the nucleophilic substitution route could be more likely.

It can be clearly seen by comparing table 3.5.2 (the observed experimental NMR data for the reaction of $P_3N_3Cl_6$ with glycidol) with tables 3.5.3 and 3.5.4 that the information presented resembles more closely the data from the reaction of 1,3-

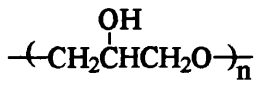
propanediol with $P_3N_3Cl_6$, thus indicating that nucleophilic attack of the epoxide ring onto the phosphazene ring is occurring. The evidence points to the fact that simple substitution to give the mono substituted product is occurring (or possibly the bridged species, 22 - 22.5ppm and 14.5 - 15.5ppm in the ^{31}P NMR) and this is happening under all conditions tried. However, when more glycidol was introduced to the system in an attempt to fully substitute the phosphazene ring the NMR data pointed to more side reactions occurring with the subsequent formation of the six membered spirocyclic material. (23.7ppm and 5.4ppm in the ^{31}P NMR, 67.85ppm and 25.45ppm in the ^{13}C NMR and 4.36ppm with 2.17ppm in the ^{1}H NMR). There may also be the formation of a fully substituted spirocyclic material in the 1:6 reaction (17.5ppm in the ^{31}P NMR, reported as 14ppm by Shaw *et al* for the reaction of 1,3-propanediol) however, this seems strange as no indication of the formation of the intermediate bi-substituted spirocyclic moiety can be found.

This suggested solution does not account for all of the observed signals however, and to try to explain what other products may be being formed polymerisation of the glycidol, either prior to, or following substitution of the phosphazene ring, must again be considered. Early work on the base polymerisation of glycidol reported the production of a low molecular weight, linear polyglycidol which was obtained via a 1,3 polymerisation route.[210] However, later studies discussed the possibility that a rearrangement polymerisation route existed which yielded largely a 1,4 - poly(3-hydroxyoxetane).[211] Following the formation of the glycidoxy anion it was believed that propagation involved attack on the ring CH_2 carbon to generate a secondary oxyanion which then, due to proton transfer, rearranges to a primary oxyanion. Scheme 3.5.2.

Scheme 3.5.2.

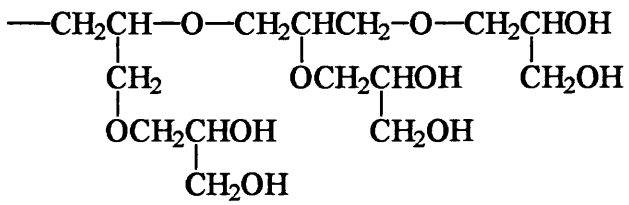


This mechanism would be expected to yield a linear polymer with the general structure (XLVI).



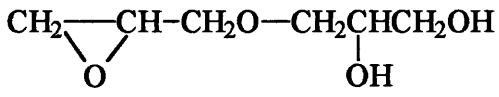
(XLVI)

Proton exchange with other hydroxyl groups along the chain or from glycidol molecules and propagation involving the secondary oxyanion results in a great deal of branching along this backbone. (XLVII)



(XLVII)

In addition to polymer, a significant amount of dimer, (XLVIII), was also observed in the polymerisation of glycidol.



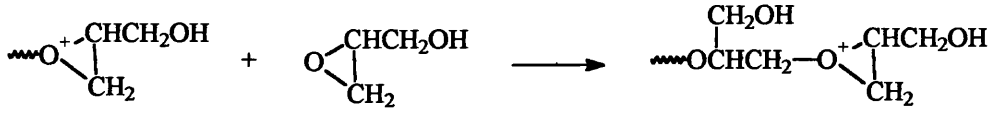
(XLVIII)

The ^{13}C NMR data observed for this product is given in table 3.5.5.

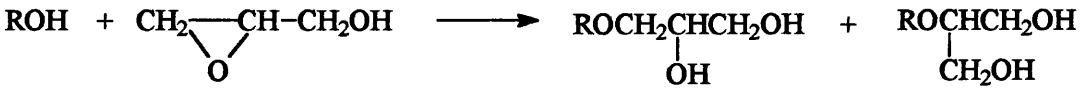
More recently the cationic polymerisation of glycidol has been described in terms of two competing mechanisms, an active chain end mechanism, (ACE), and an activated monomer mechanism, (AM).[212]

The ACE mechanism, consisting of nucleophilic attack of the monomer on a tertiary oxonium ion active species in the polymer would be expected to yield only [$CH_2CH(CH_2OH)O$] repeat units and the AM mechanism, which consists of attack of a hydroxyl group of the polymer on a protonated monomer, to yield both [$CH_2CH(CH_2OH)O$] and [$CH_2CH(OH)CH_2O$] repeat units. Scheme 3.5.3.

Scheme 3.5.3. The ACE mechanism.



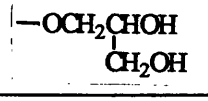
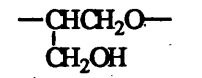
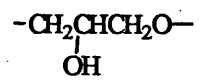
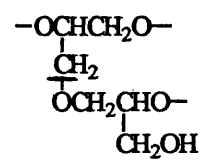
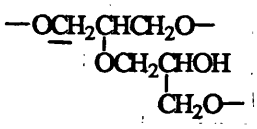
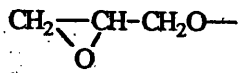
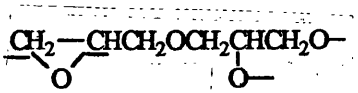
The AM mechanism.



Depending upon how the ring opens in the ACE mechanism combinations of head, tail sequences may be observed. These two mechanisms may be distinguished in the final polymer from observations of the type of hydroxyl groups present in the chain, the ACE mechanism gives only primary groups whereas the AM mechanism gives both primary and secondary. Again branching could be expected to occur, if a side group hydroxyl unit participated in the AM mechanism.

This previous work allows the ^{13}C NMR assignments for various groups in the expected products to be given. Table 3.5.6.

Table 3.5.6 ^{13}C NMR data for various units within the expected product from the polymerisation of glycidol.[212]

Unit	Carbon atom	Chemical shift (ppm)
end group 	-O-CH_2- -CH-OH CH_2OH	72 70 62
chain unit 	-CH- -CH_2-O- -CH_2OH	78 68 60.5
chain unit 	-CH_2- -CH-	72 68
branch 	-CH_2- -CH- -CH_2-O-	70.8 78 68.8
branch 	-CH- -CH_2-	78 70
end group 	-CH_2- -CH- -CH_2-O-	44.8 51.5 71.5
glycidol dimer [a] 	-CH_2-O-$SiMe_3$ -CH($OSiMe_3$)- -CH(O)- -CH_2(O)-	64.2 72.3, 72.1, 72.0[b] 50.7 44.3

(a) The ^{13}C NMR for this material was run on the trimethylsilyl ether of the dimer.

(b) Three signals were observed due to the presence of three diastereoisomers.

As glycidol has been shown to undergo both cationic and anionic polymerisation it seemed very likely that the conditions within the reaction system would be sufficient to initiate the polymerisation of at least some of the glycidol reagent in the reaction. This idea was tested by performing 'control' reactions of stirring glycidol and a mixture of glycidol with Na_2CO_3 under the same conditions as those in the substitution reactions.

The observed ^{1}H and ^{13}C NMR data for these reactions is presented in table 3.5.8.

When compared with table 3.5.6 it can be seen that many of the signals in table 3.5.8 could be assigned to a number of different structural units and hence it is very difficult to say exactly what materials are present in the systems.

It is obvious that some form of polymerisation is occurring under the reaction conditions employed although to what extent this proceeds is unclear, it could be that only the dimer, glycidyl glycerin (XLVIII), is formed or it may be that a polyglycidol is formed along with this dimer. Whichever of these is the case it is clear from the NMR data presented in table 3.5.2 that further potential nucleophiles are present in the phosphazene reaction systems and so are leading to a complicated mixture of products. Table 3.5.7. shows the amounts of the identifiable products present. Due to the irreproducibility of the reactions, for example the amount of unreacted $P_3N_3Cl_6$ varied between 27 and 65%, these amounts are the average over three reactions.

Table 3.5.7

Product	% Product
Unreacted $P_3N_3Cl_6$	46
monosubstituted	10
spiro-cyclic material	4
other[a]	27

(a) Others refers to identifiable patterns within the spectra which could not be assigned as a definite product. i.e. those products thought to arise as a result of the polymerisation of glycidol.

Table 3.5.8.

Reaction	^1H	^{13}C
Glycidol + Na_2CO_3	epoxide CH_2 2.81ppm (d of d), J=4.76 Hz. 2.73ppm (d of d), J=2.75Hz, J'=4.7 Hz. epoxide CH 3.17ppm (m) -CH_2-O- ~ 3.6ppm and 3.95ppm very broad, unresolved signals. polymer CH(O) 3.75ppm (m), broad polymer -CH_2-O- 3.6 - 3.9ppm	unreacted glycidol 61.93ppm epoxide CH 52.25ppm -CH_2-O- 44.14ppm epoxide CH_2 others 71.52ppm 70.68ppm 67.74ppm 67.37ppm 63.53ppm 57.89ppm 50.69ppm 43.99ppm
Glycidol stirred	epoxide CH_2 2.8ppm (d of d), J=4.1 Hz 2.74ppm (d of d), J=2.75 Hz., J'=4.8 Hz epoxide CH 3.17ppm (m) -CH_2-O- ~ 3.9ppm and 3.6ppm, broad, unresolved multiplets polymer CH(O) 3.75ppm (m), broad polymer -CH_2-O- 3.6 - 3.9ppm	unreacted glycidol 61.96ppm epoxide CH 52.30ppm -CH_2-O- 44.21ppm epoxide CH_2 others 71.57ppm 70.63ppm 67.81ppm 67.48ppm 63.60ppm 58.04ppm 50.76ppm 44.05ppm

This work has shown that the reaction of $P_3N_3Cl_6$ with glycidol results in a complex mixture of products, mainly as a result of numerous side reactions which occur along with the expected substitution reaction. This mixture has been shown to consist of the expected monosubstituted phosphazene, various products from further nucleophilic attack of the oxirane oxygen atom such as a bridged phosphazene species

and a phosphazene bearing a spirocylic ligand. Evidence has also been provided for the formation of substituted phosphazenes bearing glycidol side groups which have undergone varying degrees of polymerisation.

It was decided, following these studies of the conventional reaction of $P_3N_3Cl_6$ with glycidol, to study also the ultrasonic reaction in the hope that the system may be simplified.

CHAPTER 4

THE APPLICATION OF ULTRASOUND TO THE SUBSTITUTION REACTIONS OF CYCLIC PHOSPHAZENES

A selection of the reactions studied under more conventional conditions were chosen to be studied under sonochemical conditions. These were the reactions of $P_3N_3Cl_6$ with p-cresol, trifluoroethanol, the Grignard reagents and glycidol which were chosen mainly for the variety of type of ligand (i.e. aryloxy, alkoxy, organometallic and a 'bifunctional' reagent) but also for the variety of different substitution levels displayed in the p-cresol system and and the competition between two different reaction mechanisms in the Grignard systems. The 2,4,6-tri-t-butylphenol reaction was omitted partly due to its similarity to the p-cresol ligand, but, mainly due to the irreproducibility and complexity of the reaction displayed under conventional conditions.

From reactions described in the literature[147, 148, 149] it was expected that properties such as greater yields of products, more highly substituted products due to the reaction proceeding further and maybe even one type of product predominating over another due to a preference for a particular reaction mechanism would be observed.

Work carried out by Luche *et al*[212] on predicting the effect of ultrasound on chemical reactions has led to the development of a set of "rules".

- In homogeneous solution the application of ultrasound favours single electron transfer processes. Purely ionic reactions should not be affected.
- In heterogeneous (liquid-liquid or liquid solid) systems, ionic reactions can be stimulated by the mechanical effects of ultrasound. The nature of the products obtained, however, will be the same as in the absence of ultrasound.
- In heterogeneous systems, those reactions which can follow either an ionic or an electron transfer pathway will be induced to react preferentially via the electron transfer pathway.

The result of these rules is that, for the reaction systems studied in this work, the following predictions were made.

The reaction of $P_3N_3Cl_6$ with the sodium salts of both p-cresoxide and trifluoroethoxy species is known to follow a nucleophilic substitution mechanism,[45] i.e. an ionic pathway. As these reactions were carried out in homogeneous solution it would be expected that no effect would be observed upon sonication.

A very similar situation exists in the reaction of $P_3N_3Cl_6$ with glycidol. Nucleophilic substitution is the expected mechanism, however, in this case the reaction was carried out in the presence of solid Na_2CO_3 i.e. a heterogeneous mixture. This means that some mechanical effects (possibly resulting in higher yields) of the application of ultrasound would be expected. These effects would also be expected to be observed in the many side reactions described in the system, section 3.5, (further

nucleophilic attack of the epoxide oxygen atom on the phosphazene ring and polymerisation of the glycidol) as these too are ionic processes.[208, 211] This would have the result that the system would be expected to be just as complicated as that of the conventional reaction.

The reaction between $P_3N_3Cl_6$ and Grignard reagents is described as following both nucleophilic substitution and metal halogen exchange pathways.[66b] Although this metal halogen exchange pathway has been shown to be occurring, it is not yet known whether it follows an ionic or a radical mechanism.[66b, 213] The application of ultrasound to this system would seem to provide a possible method of obtaining further information to help solve this problem.

The reactions PhMgCl and ^{t}-BuMgCl were both carried out in homogeneous solution with the result that the nucleophilic substitution pathway (yielding the monosubstituted phosphazene product) would be expected to be unaffected. This means that no difference to the observed products etc. would be expected in the reaction with ^{t}-BuMgCl. Also, if the metal - halogen exchange pathway was ionic in nature, as might be expected from the vast majority of Grignard reactions[214] then again, no effect upon sonication of the reaction would be expected. This would be observed in the PhMgCl system.

If, on the other hand, the metal - halogen exchange process was radical in nature (as would be suggested from common organometallic reactions[215]) then this could be observed as a change in the product type, or as a significant increase in the amount of the bi(cyclophosphazene) product in the PhMgCl reaction.

4.1 REACTION WITH P-CRESOL

Both the 1:1 and 1:2 stoichiometry reactions were carried out under the influence of ultrasound (administered via the VC50 ultrasonic probe system, see section 2.5.1 for experimental details) and in both cases a tendency toward higher levels of substitution was observed. This is displayed in Table 4.1.1. and in Figures 4.1.1 and 4.1.2.

It can be clearly seen that in the 1:1 reaction, where previously no tri-substituted product was observed, the use of ultrasound resulted in the formation of a substantial amount. Also, in the 1:2 reaction a significant rise in the amount of higher substituted products was observed, even if no higher levels were attained. These observations are clearly in contrast to the expected results of applying ultrasound to this system.

The reasons for these unexpected observations were believed to be due to the higher temperatures usually attained in ultrasonic reactions along with the efficient agitation set up by the ultrasonic cavitation process.

Table 4.1.1. Product distribution for the ultrasonically controlled reaction of $P_3N_3Cl_6$ with p-cresol

Stoichiometry	Compounds observed	% of Total cyclic products
1:1	$P_3N_3Cl_6$	14
	monosub	18
	bisub (ng)	40
	(g)	2
	trisub (ng)	21
	(g)	5
1:2	monosub	16
	bisub (ng)	65
	(g)	3
	trisub (ng)	13
	(g)	3

These ideas were tested by monitoring the temperature within the reaction vessel during both a conventional and ultrasonic reaction, of 1:1 $P_3N_3Cl_6$ with p-cresol, carried out under the same conditions. It was found that the temperature within the reaction vessel in the ultrasonic reaction was approximately 4 to 5°C higher than that reached in the conventional reaction vessel.

The conventional reaction was then repeated under conditions designed to give the same reaction temperature as was measured in the ultrasonic reaction. The product distributions (as well as the observed reaction temperatures) are given in Table 4.1.2. and shown in Figure 4.1.3.

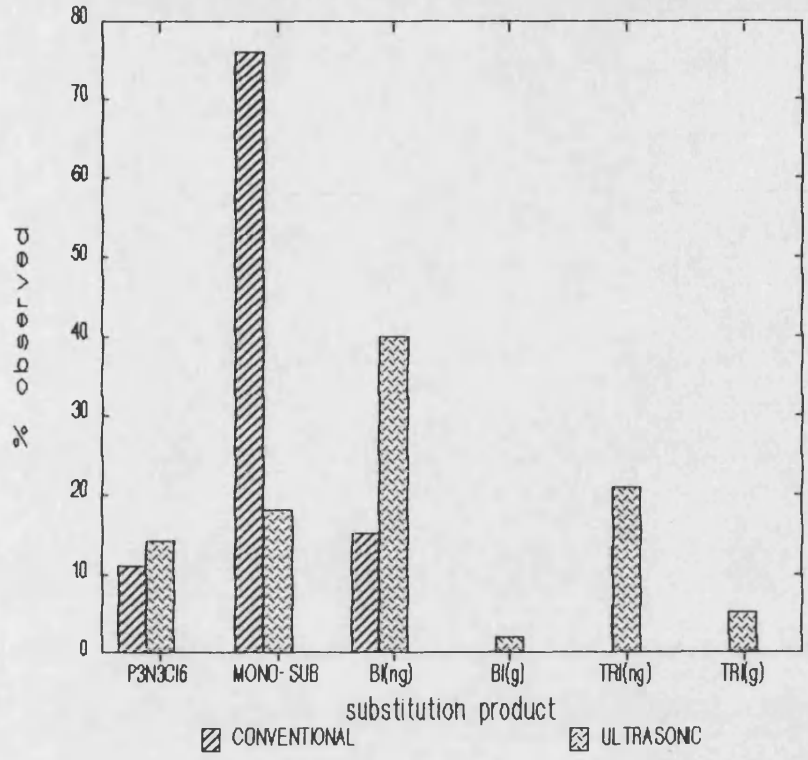


Figure 4.1.1 Product distribution (%) for the conventional and ultrasonic 1:1 reaction of $P_3N_3Cl_6$ with p-cresol.

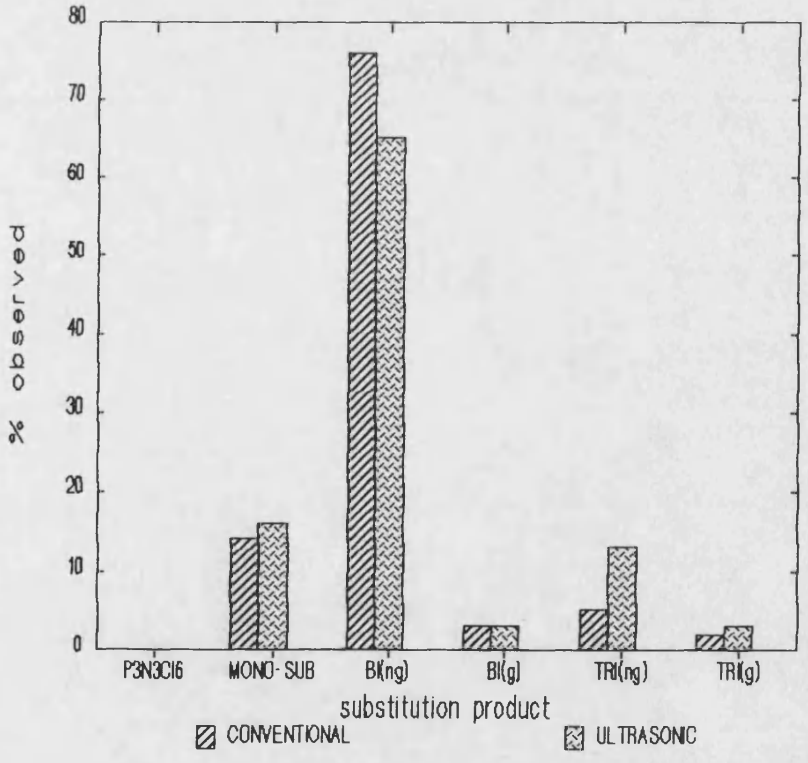


Figure 4.1.2. Product distribution for the conventional and ultrasonic 1:2 reaction of $P_3N_3Cl_6$ with p-cresol.

Table 4.1.2.

Product	% Products		
	Conventional (303K)	Ultrasonic (303K) [measured 308K]	Conventional (308K)
$P_3N_3Cl_6$	27	9	3
monosub	68	69	70
bisub (ng)	5	22	27

The obvious similarities between the ultrasonic and the higher temperature, conventional reaction product distributions, indicate that the ultrasound is indeed resulting in a higher reaction temperature and that this is the reason for the change in the product distribution rather than any chemical effects. This is clearly in agreement with the predictions made at the beginning of this chapter concerning this reaction system and provides another example to further corroborate the "rules" of Luche *et al.*[212]

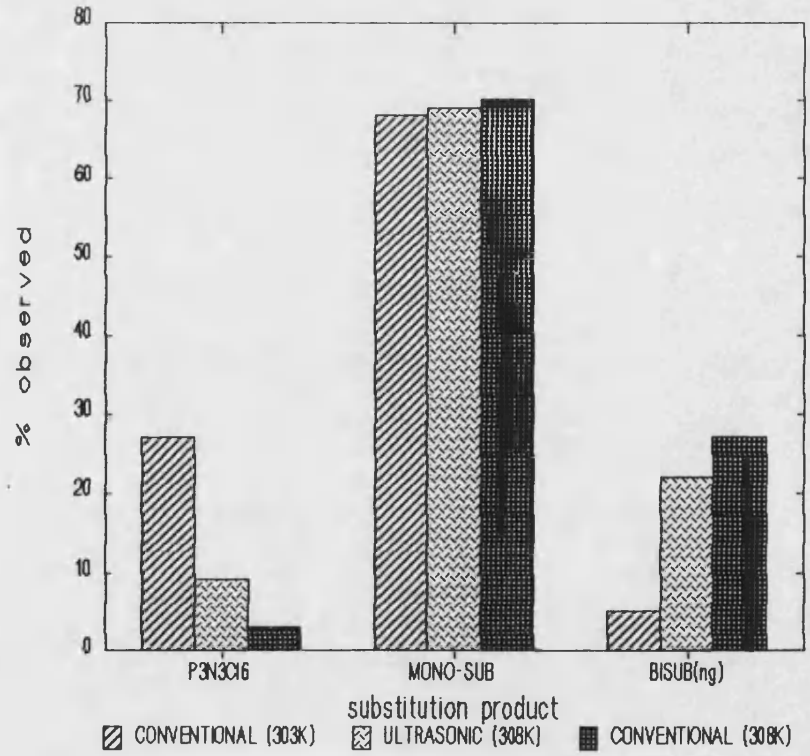


Figure 4.1.3 Product distribution for the variable temperature 1:1 reactions of $P_3N_3Cl_6$ with p-cresol.

4.2 REACTION WITH TRIFLUOROETHANOL.

The observations made of the effect of ultrasound within the p-cresol reaction system were repeated in the trifluoroethanol system, that is, when ultrasound was used more of the higher levels of substitution were observed. Table 4.2.1. Again this is unexpected

Table 4.2.1.

Products observed	% product
$P_3N_3Cl_6$	35
monosub	27
bisub (trans)	26
(cis)	2
trisub (ng)	7

Work carried out by Schmutz and Allcock[45b] showed that as the reaction temperature was raised in the conventional reaction, more of the higher substituted products were observed and also some cis isomer of the bi-substituted product was observed. When considered in conjunction with the fact that additional products were observed in this work when ultrasound was present in the reaction system the argument that ultrasound has the effect it does by raising the reaction temperature would seem to apply to this system as it did in the p-cresol system.

The ^{31}P NMR data for the additional products observed are given in Table 4.2.2.

Table 4.2.2. ^{31}PNMR data for the additional products observed in the ultrasonic reaction of $P_3N_3Cl_6$ with trifluoroethanol.

Compound	δPCl_2	$\delta PCl(OR)$	$^2J_{PP}$ (Hz.)
bisub (ng) [a]	23.7	18.1	67.9 to 69.9
trisub (ng)		21.5 to 21.7 (m) [b]	

(a) Signals were observed as a smaller doublet - triplet pattern shifted slightly from the larger trans isomer signals. These were assumed to be due to the cis isomer of the bi-substituted product based upon the arguments presented by Schmutz and Allcock for a trans, non-geminal pathway and on similar observations made in the p-cresol system. (Figure 3.1.1).

(b) The multiplet observed appeared to consist of an overlapping triplet and doublet which would be expected from an AA'_2 spectrum such as that of the non-geminal, trans isomer of the trisubstituted product.

4.3 REACTION WITH GRIGNARD REAGENTS.

It might now be expected, from what was observed in both the p-cresol and trifluoroethanol systems, that the predictions made at the beginning of this chapter concerning the two Grignard systems would need to be altered. The effect of raising the temperature in the conventional reaction of various Grignard reagents with $P_3N_3Cl_6$ has been shown[66b] to be an increase in the amount of nucleophilic substitution observed. In those systems in which both nucleophilic substitution and metal - halogen exchange compete it has been noted that there is a rise in the amount of mono-substituted product and a drop in the amount of bi(cyclophosphazene) formed during the reaction. This effect, however, would be expected to be minor in comparison with any observed mechanistic effects that the introduction of ultrasound may have and so it would be expected that the earlier predictions would still hold.

In each of the reactions carried out the same products as observed in the conventional reactions were observed and the amounts of the various products obtained are shown in Tables 4.3.1. and 4.3.2.

Table 4.3.1. Product distribution for the reactions of $P_3N_3Cl_6$ with t-BuMgCl

Reaction	$P_3N_3Cl_6$	$P_3N_3Cl_5$t-Bu	$P_3N_3Cl_5(OC_3H_7)$	Rearranged products	Unidentified products
Conventional	75 (89)	12	8	2	4
Ultrasonic	61 (75)	25	10	3	1

The values in parentheses are the corrected values (see Section 3.3.)

There appears to be a small effect upon the reaction of $P_3N_3Cl_6$ with t-BuMgCl. A significant rise in the amount of mono-substituted product was observed (however, the total amount of this material observed remained small) along with a small increase in the total amount of identifiable products, however, as the calculation of the amounts of product were based on the integration of the NMR spectra a change of less than 5% can reasonably said to be a constant value.

This observation is as expected as at least a slight increase in the amount of mono-substituted product would have been expected due to the temperature effect of sonication described for the p-cresol and trifluoroethanol systems. When it is realised, however, that the change in temperature was only actually 4 to 5°C from that of the conventional reaction (as in the p-cresol reactions) and that there would be a fairly large steric barrier to the substitution of a chlorine atom on the phosphazene ring by a

large t-butyl group it is perhaps not surprising that only a small amount of monosubstituted material is observed.

The amounts of the various products obtained in the reaction with PhMgCl are shown in Table 4.3.2. and in Figure 4.3.1.

Table 4.3.2 Product distribution in the ultrasonic reaction of $P_3N_3Cl_6$ with PhMgCl

Time (hrs.)	$P_3N_3Cl_6$	$[P_3N_3Cl_4(Ph)]_2$	$P_3N_3Cl_5(OC_3H_7)$	Rearranged products
1	21 (100)		79	
2	24 (98)	1.7	45	29
3	13 (98)	1.8	62	23
6	23 (99)	1.6	50	26
10	16 (99)	1.7	45	38
20	23 (99)	2.2	51	26
26	27 (98)	2.1	47	24

The values in parentheses are the corrected values (Section 3.3)

It can be seen that much less bi(cyclophosphazene) was observed in the ultrasonic reaction than in the conventional reaction (Section 3.3). When the predictions made are considered, this is unexpected as the results do not appear to support either of the mechanisms proposed. Several possible reasons for these observations have been considered.

Observations made in the reactions of $P_3N_3Cl_6$ with both p-cresoxy and trifluoroethoxy ligands have shown that ultrasound gives results equivalent to a rise in temperature in the reaction system, and that this in turn results in greater nucleophilic substitution. If this was occurring in this system then a fall in the amount of the bi(cyclophosphazene) observed might be expected. This is clearly not occurring as no monosubstituted product (that which might be expected from an increase in any nucleophilic substitution) is observed in any of the analytical data. Indeed, a rise in temperature in this reaction system has been shown[66b] to have no effect on the nature, or the amounts of products observed from this reaction.

It is known that bi(cyclophosphazenes) may be cleaved across the P-P bridging bond, for example in the reaction with nucleophiles[198, 199], and as discussed in Chapter 1 ultrasound has been used to cleave bonds in such things as polymers. It may be that the ultrasound is causing the cleavage of some of the bi(cyclophosphazene) with the result that more cyclic products are observed. If this was the case it would be expected that phenyl substituted cyclic phosphazenes would be observed in the final product mixture. These products are not observed, thus this possibility can be discounted.

The possibility exists that the ultrasound may be affecting the Schlenk equilibrium and that this may be affecting the production of the bi(cyclophosphazene) product. This is unlikely, however, as Allcock et al[66b] investigated the effect of altering the Schlenk equilibrium on the reaction of $P_3N_3Cl_6$ with Grignard reagents and found that no influence was exerted.

The only other possibility which seems feasible is that of the ultrasound affecting the equilibrium between the unreacted $P_3N_3Cl_6$ and the metallophosphazene intermediate (Scheme 3.3.1). It is reasonable to assume that the weakest bond in the intermediate is that between the cyclic nitrogen atom and the magnesium ion, it is possible that ultrasound is causing a 'push' toward the unreacted $P_3N_3Cl_6$ in this equilibrium thus resulting in the formation of substantially less bi(cyclophosphazene) product. At this stage, however, this is pure postulation and a significant amount of further work is required in this area in order to clarify the effects of the ultrasound on this reaction. For example, although no similar stable phosphazene anion has been isolated, a similar material containing a lithium counterion has been studied using low temperature ^{31}P NMR[216a] and it may be possible to identify the effects of ultrasound on this material. These phosphazene anions have also been 'trapped' using electrophiles[66b,216a] such as R'Cl and PrOH, it may be possible to follow the effects of ultrasound on the formation of the phosphazene anion by studying these materials.

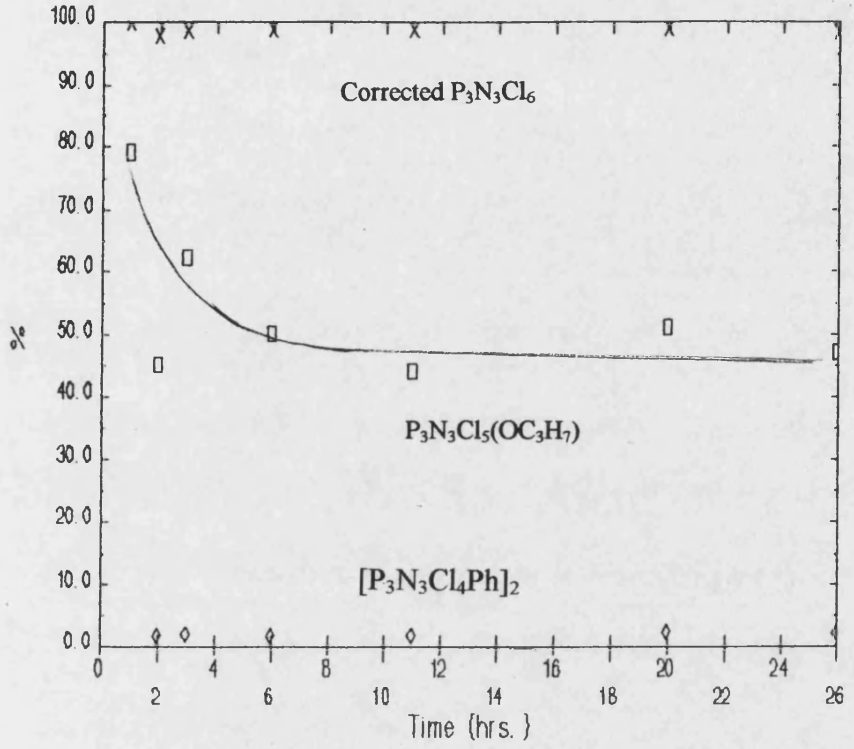


Figure 4.3.1. Distribution of products in the ultrasonic reaction of $P_3N_3Cl_6$ with PhMgCl.

4.4. REACTION WITH GLYCIDOL.

From predictions made at the beginning of this chapter it would be expected that in this system a larger amount of the mono-substituted product and the spirocyclic product would be formed, however, similar trends would also be expected from the various side reactions observed in the conventional reactions.

Inspection of the NMR spectra revealed that the same species had indeed been formed, again in what appeared to be a complex mixture, however, there seemed to be less of these materials present. It was also noted that a large increase in the amount of unidentified material had occurred. There was again a large degree of irreproducibility in the spectra obtained and in the amounts of the products which could be identified.

The relevant product distributions are given in Table 4.4.1. which shows the average amounts over three reactions. (An average amount is displayed because of the severe irreproducibility of these reactions, for example, the amount of the spirocyclic product observed in each of the three reactions referred to was 1, 3.7 and 9%)

Table 4.4.1.

Product	% Product
unreacted $P_3N_3Cl_6$	27
monosubstituted	2
spiro-cyclic material	5
other [a]	52

(a) Other refers to identifiable patterns within the spectra which could not be assigned as a definite product.

This is clearly not in agreement with the predictions made and would seem to contradict the "rules" of the effects of ultrasound on chemical reactions, however, a simple explanation exists for these observations. The increase in the amount of unidentified materials present can be put down to the fact that as the reaction temperature was raised by the ultrasound then more polymerisation of the glycidol would occur, thus leading to a higher proportion of reactions involving either the glycidol dimer or polyglycidol rather than the glycidol itself. This would also result in the corresponding observed drop in the amount of mono-substituted and spiro-cyclic materials formed due to the increased amounts of glycidol being involved in the polymerisation reactions.

This chapter has described the first applications of ultrasound to phosphazene chemistry. The work carried out has shown that the prediction "rules" suggested by

Luche *et al*[212] generally hold although, often, additional factors such as side reactions (as in the glycidol reaction system) must be taken into consideration when explaining any observed effects.

It has been shown that sonication of substitution reactions of phosphazenes generally leads to higher levels of substitution and to greater yields of actual substitution products. This has the possibility of applications at the high polymer level. The use of ultrasound has the potential in the formation of more fully substituted polyphosphazenes which could result in less cross-linking (generally attributed to the high reactivity of the P-Cl bonds in poly(dichlorophosphazene)) of the polymers.

Ultrasound has been used as a tool to attempt to shed light on a reaction mechanism which has puzzled workers in the field for a number of years. The work carried out has proved to be rather inconclusive, although, evidence suggests that the metal - halogen exchange pathway which leads to the formation of the bi(cyclophosphazenes) in reactions of $P_3N_3Cl_6$ with Grignard reagents is ionic in nature. Ultrasound has been observed to suppress the formation of the phenyl substituted bi(cyclophosphazene), if this was to be observed in reactions with other Grignard reagents then the possibility exists that ultrasound would have useful applications in polymer substitution reactions. Because the bi(cyclophosphazene) products are formed in reactions with Grignard reagents it has been suggested that the high amounts of cross - linking observed in reactions of these materials with poly(dichlorophosphazene) is due to P-P bond formation.[66b] The application of ultrasound to these reactions has the potential to suppress this cross - linking and thus result in 'cleaner' substitution of the polymer.

A potential drawback to the proposed application of ultrasound to polyphosphazene reaction systems is the fact that ultrasound has been observed to result in the degradation of organic polymers[169], the potential for ultrasound to do this in polyphosphazene systems is discussed in the next chapter.

CHAPTER 5

PHOSPHAZENE POLYMER CHEMISTRY

As discussed in Chapter 1 a number of synthetic routes exist to polyphosphazenes, each of which results in a polymer with properties dependent upon the method of synthesis employed. For example, condensation polymerisation of N-silylphosphoranimines tends to result in polymers with fairly low molar masses (~ 50,000) whereas bulk or solution polymerisation at temperatures of up to ~ 250°C can yield polymers with molar mass of up to several million. Only limited control of these properties is possible within each synthetic route.

Ultrasound has been used to help control the synthesis of a variety of both organic and inorganic polymers and copolymers[217], for example, Shen et al[218] found that by altering the sonication time copolymers of poly(vinyl acetate) and polyacrylonitrile could be formed which were either water soluble or insoluble as desired and the control of the molar mass distribution of polysilanes during sonochemical synthesis has been found to be possible by altering the intensity of the ultrasound employed in the synthesis.[217]

For the purposes of this study it was thought that if ultrasound could be employed in the synthesis of polyphosphazenes then greater control over the properties of the resulting polymers might be achieved. Based upon observations made at the small, cyclic molecule level, i.e. because they gave the most consistent results as well as being the clearest systems (in terms of identification of products), it was decided to synthesise polymers with $OC_6H_4CH_3$-p and OCH_2CF_3 side groups.

5.1 CONVENTIONAL POLYMERISATIONS

The first attempts to synthesise polydichlorophosphazene were based upon a method described by Allcock[14] in which $P_3N_3Cl_6$ was heated to 250°C in a sealed, evacuated polymerisation ampoule.

Attempts were carried out which were both uncatalysed and catalysed with either ethanol or benzoic acid. These attempts had only a very limited success with the major product isolated being an insoluble, gel-like material (~ 95%) and only trace amounts of a soluble polymeric material being obtained. It is believed that this insoluble material is cross - linked polydichlorophosphazene leading to the conclusion that insufficient control over atmospheric moisture, impurities and polymerisation temperature was obtained during the polymerisations.

It was then thought that more control might be possible if polymerisation were to be carried out in solution. The method chosen was as described by Magill et al.[191] and consisted of 1,2,4-trichlorobenzene solvent, sulfamic acid catalyst and $CaSO_4 \cdot 2H_2O$ promoter.

Appropriate temperature control allowed the production of polymer in significant amounts. This method of synthesis yielded polymer (to approximately 50 - 60% conversion levels from the cyclic trimer, $P_3N_3Cl_6$, which was as quoted in the literature[191]) which was a dark brown (due to thermal decomposition of the catalyst during synthesis), THF soluble elastomer. This soluble $(NPCl_2)_n$ was used in substitution reactions with either $-OC_6H_4CH_3$-p or $-OCH_2CF_3$ within 24 hours of its formation in order to minimise the likelihood of cross-linking. The analytical data for the resulting polymers is shown in Table 5.1.1.

At this point it is perhaps appropriate to comment on the analytical procedure used when carrying out the gel permeation chromatography.

In the GPC analysis of the synthesised polymers, low polydispersity, polystyrene standards were used to produce a calibration curve. As discussed in Chapter 1 this may not result in the determination of true values of the molar mass as for the most accurate results, known standards of the polymer under analysis should be used. Also, as values for the Mark-Houwink constants for the polymers under analysis are not known, the Universal Calibration is not a viable option.

As a result, the values of the molar masses which have been determined are quoted as a 'polystyrene equivalent'. The fact that these may be considerably different from the true values is not really important as essentially only a qualitative idea of any trends is needed at this stage. As all of the analyses were carried out in an identical manner, comparisons of the values obtained for samples of the same polymer system which have undergone sonication under various conditions is a legitimate procedure. Any comparisons made between different polymer systems, however, may not be.

Analysis conditions

During analysis of the sonicated samples of polymer it was noticed that the values of the molar masses, obtained by GPC, were affected by the concentrations of the sample solutions being injected.

This is demonstrated in Table 5.1.2 and in Figure 5.1.1 for the $[NP(OC_6H_4CH_3)_2]_n$ polymer.

Table 5.1.1 Analytical data for polymers obtained from solution polymerisation.

Polymer	NMR Data			GPC Data	DSC (°C)	Elemental					
						calculated (%)			measured (%)		
	^{31}P	^{1}H	^{13}C			C	H	N	C	H	N
$[NP(OC_6H_4CH_3)_2]_n$	-19.6	6.65 - 6.75 (m) 2.1 (s)	149.3 132.0 129.25 121.01 20.61	196000 - 278000	Tg = -2.8	64.87	5.44	5.40	60.5	5.15	5.66
$[NP(OCH_2CF_3)_2]_n$	-8.36			63000 - 73000	Tg = -65.4	21.16	1.78	6.17	19.7	1.67	5.77

Table 5.1.2: Variation in M_n for various concentrations of $[NP(OC_6H_4CH_3)_2]_n$ solution analysed by GPC.

Concentration (w/v)	Mn
5%	85700
1%	184900
0.7%	182900
0.5%	195500
0.3%	198200
0.15%	219100
0.1%	277800
0.07%	288900
0.05%	293000
0.03%	257000
0.01%	273800

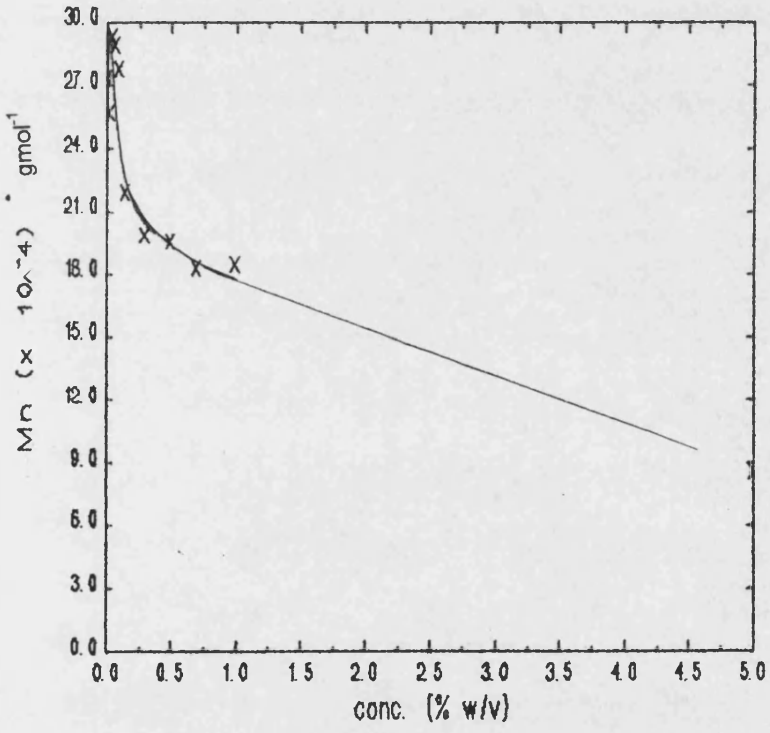


Figure 5.1.1: Graph of the variation of M_n vs. conc. for various concentrations of $[NP(OC_6H_4CH_3)_2]_n$ solution.

The data shown indicates that if a more concentrated sample was injected then a lower value of the molar mass was obtained. This phenomenon was also displayed in the $[NP(OCH_2CF_3)_2]_n$ polymer system as is demonstrated by Figure 5.1.2.

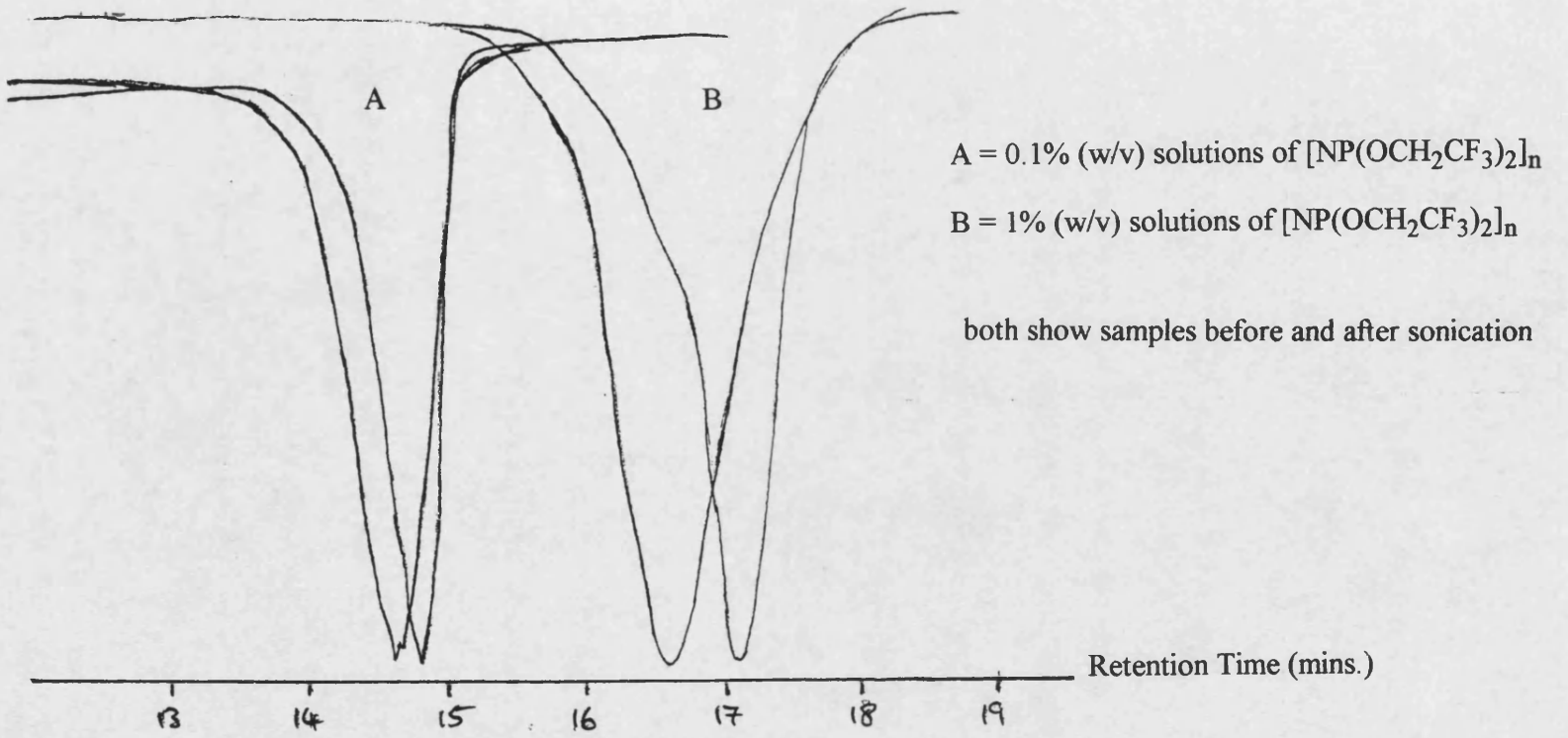


Figure 5.1.2: Some example chromatograms of $[NP(OCH_2CF_3)_2]_n$ polymer showing that lower concentrations elute at lower times thus indicating higher molar masses.

Although the values of the molar masses are changing by quite a considerable amount over the range of concentrations analysed, (if it is assumed that the error in the GPC for measuring M_n is ±5% it can be seen that the observed change in M_n upon changing the sample concentration is much greater than this) it was found that any trends which were observed during a degradation were essentially unaffected. This is displayed in Figure 5.1.3 in which the change in M_n upon sonication of a 5% (w/v) solution of $[NP(OC_6H_4CH_3)_2]_n$ is shown for samples which were analysed at 5% (w/v) and 0.1% (w/v).

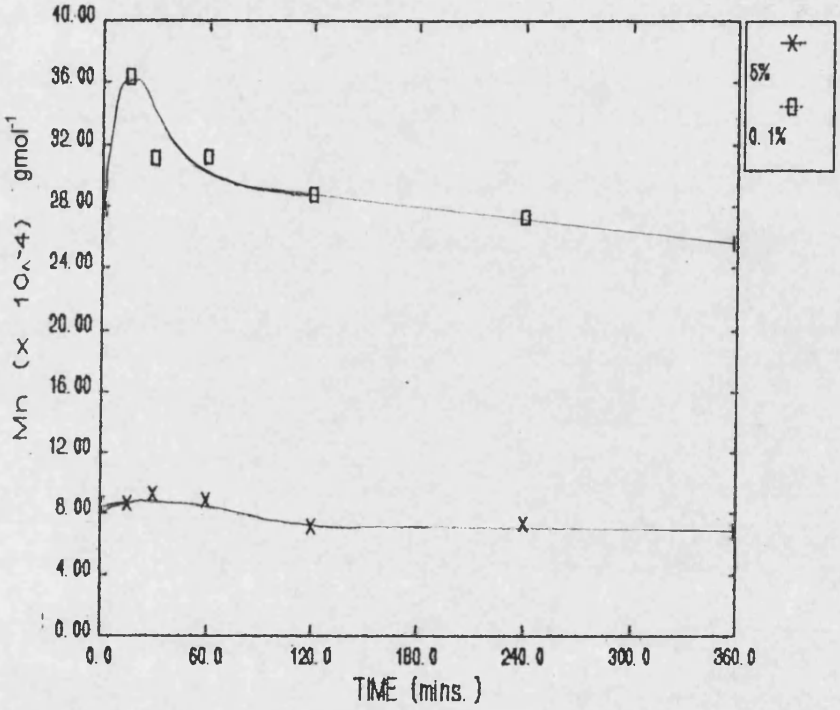


Figure 5.1.3. Effect of sample concentration upon analysis of the polymers.

The changes in the observed molar masses as the sample concentration was changed are probably due to viscosity effects, resulting in anomolous flow through the column and/or the generation of high shear forces, by the creation of high back pressures in the more concentrated solutions. These back pressures would possibly be sufficiently large to result in shear degradation of high molar mass material. Both of these effects would be expected to lead to a lowering of the observed molar mass average for higher concentrations. If the polyphosphazenes were adsorbing to the stationary phase within the column then the same effect would be observed, however, the presence of Bu_4NBr as an ionic species within the eluent is reported to prevent this and result in reproducible results.[218]

All of the above observations would seem to suggest that provided an identical analytical procedure were to be adopted in every experiment, then comparison between experiments would be legitimate. For this reason it was decided to analyse each sample as a 0.1% (w/v) solution (the concentration of the most dilute solution in the studies of the effect of concentration on the degradation of $[NP(OC_6H4CH_3)_2]_n$.

The $[NP(OC_6H_4CH_3)_2]_n$ prepared at this stage was then used in degradation experiments.

5.2 POLYMER DEGRADATIONS : THE NATURE OF THE DEGRADATION.

Of all the previous work carried out on the degradation of polyphosphazenes no mention is made of ultrasonic degradation, instead, thermal and photolytic methods seem to have predominated. A common factor in both of these methods is the loss of the initial chemical structure of the polymer. For example, the thermal degradation of $[NP(OCH_2CF_3)_2]_n$ appears to have been studied extensively[220-226] and the predominant effect reported is that of depolymerisation to cyclic phosphazenes and specifically the cyclic trimer.

The actual mechanism of the depolymerisation is still a matter of argument, however, it would appear that the method of synthesis of the initial polymer could affect it. Allcock *et al.*[220] suggested that chain scission occurred at weak points in the chain and that this was followed by rapid depropagation of the resulting species to cyclic molecules. Random chain scission was proposed by Zeldin *et al.*[221] who then suggested partial unzipping of these smaller chain species. Magill *et al.*[222] came to the conclusion that initiation of depolymerisation occurred at chain ends and that this was accompanied by some chain transfer and some chain scission at weak points in the backbone. More recently, Papkov and co-workers[223] proposed a two stage mechanism. Initial rearrangement of the backbone to form some phosphoramide areas (by the transfer of a trifluoroethyl group to a skeletal nitrogen.) followed by chain scission at those resulting weak points in the backbone. This was supported by their observation that the thermal stability of a polymer decreased as the number of phosphoramide defects in the backbone increased. White and Matyjaszewski[224] have proposed chain end initiation followed by complete unzipping of the backbone down to the cyclic trimer. They put the difference in mechanism down to the fact that their method of synthesis of the polymer (phosphoranimine condensation polymerisation - Section 4.3) resulted in no P-Cl groups being present in the backbone and hence hydrolysis to form phosphoramide defects could not occur.

Pyrolysis experiments carried out by Allen *et al*[225] have resulted in the break down of side groups to give various gaseous products and a cross-linked polymer product.

Photolysis of different types of polyphosphazenes has also given some similar results. Degradation is initially observed in the generally weaker side group bonds with the result that cross-linking of the polymer is observed. For example, Allcock et al.[226] irradiated $[NP(OC_6H_5)_2]_n$ and $[NP(OCH_2CF_3)_2]n$ with light of wavelength 254nm and observed that the molar mass of $[NP(OC_6H_5)_2]_n$ increased, as did the intrinsic viscosity of $[NP(OCH_2CF_3)_2]_n$ both indicating cross-linking. Products which would be expected from the degradation of the side groups were also observed. (e.g. C_6H_5OH, CF_3CH_3 and CO_2).

In contrast to these other types of degradation, ultrasonic degradation of a polyphosphazene has been found, in this study, to result predominantly in the cleavage of the polymer backbone. The chemical nature of the polymer was observed to be unaffected as shown in Figure 5.2.1 which shows the ^{31}P NMR spectra of a sample of $[NP(OC_6H_4CH_3)_2]_n$ prior to and after sonication and so it is assumed that the side groups remain intact.

The effect of the sonication upon the molar mass of the polymer is shown in Figure 5.2.2. and the effect upon the molar mass distribution in Figure 5.2.3.

It is generally believed that ultrasonic degradation of polymers is a non-random process, Figure 5.2.4 shows the change in the GPC chromatogram over the sonication. It can be seen that higher molar mass material (lower retention times) is lost as lower molar mass material (higher retention times) is formed and that the initially broad molar mass distribution narrows as the sonication proceeds. This would suggest that the degradation of polyphosphazenes follows the general pattern of non-random degradation.

Figure 5.2.4 also shows that the changes taking place in the molar mass are much more rapid in earlier parts of the degradation than they are in latter parts.

It might be expected that as the molar mass of the polymer is changing then the Tg of that polymer might also be affected. (As the molar mass is decreasing it would be expected that the Tg would also decrease.) This is not observed for the sonication of $[NP(OC_6H_4CH_3)_2]_n$ in this case (the Tg remained constant), however, because of the relatively small observed change compared with that which would be needed in order to observe any significant change in Tg, this observation is not a complete surprise.

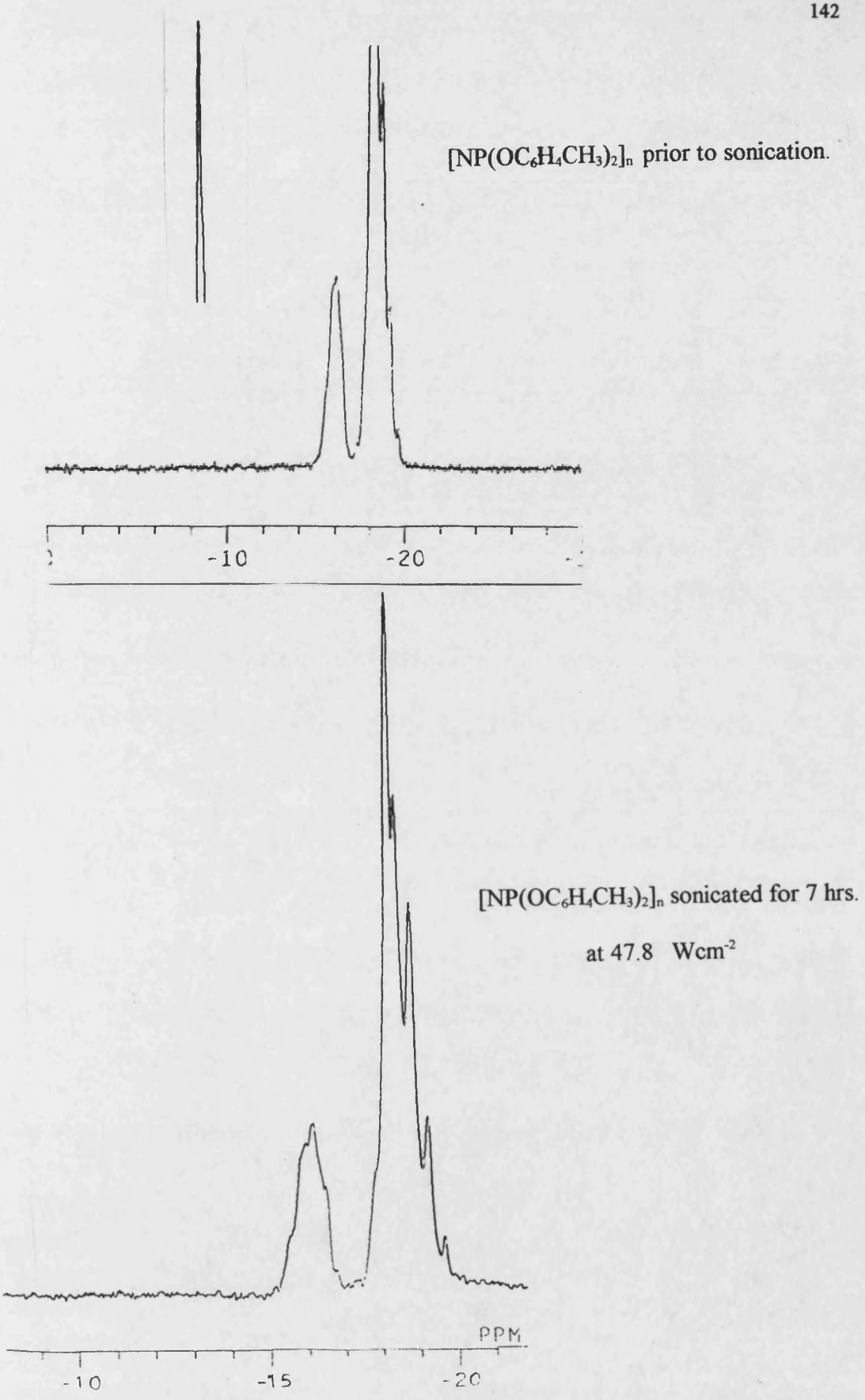


Figure 5.2.1. ^{31}P NMR spectra of p-cresol substituted polyphosphazene prior to and following sonication.

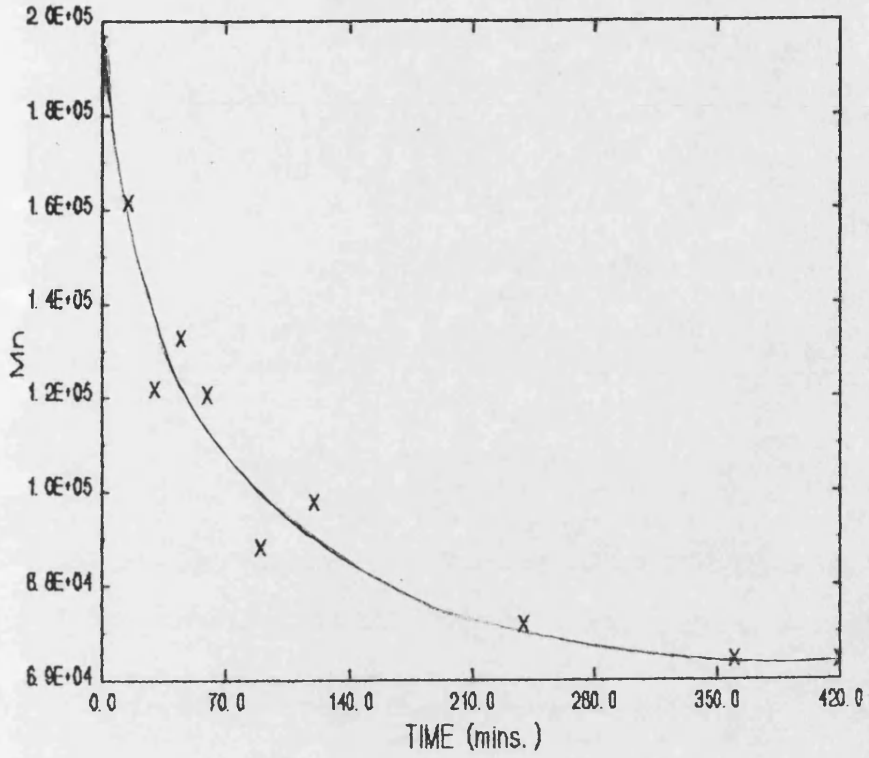


Figure 5.2.2: The effect of sonication upon M_n

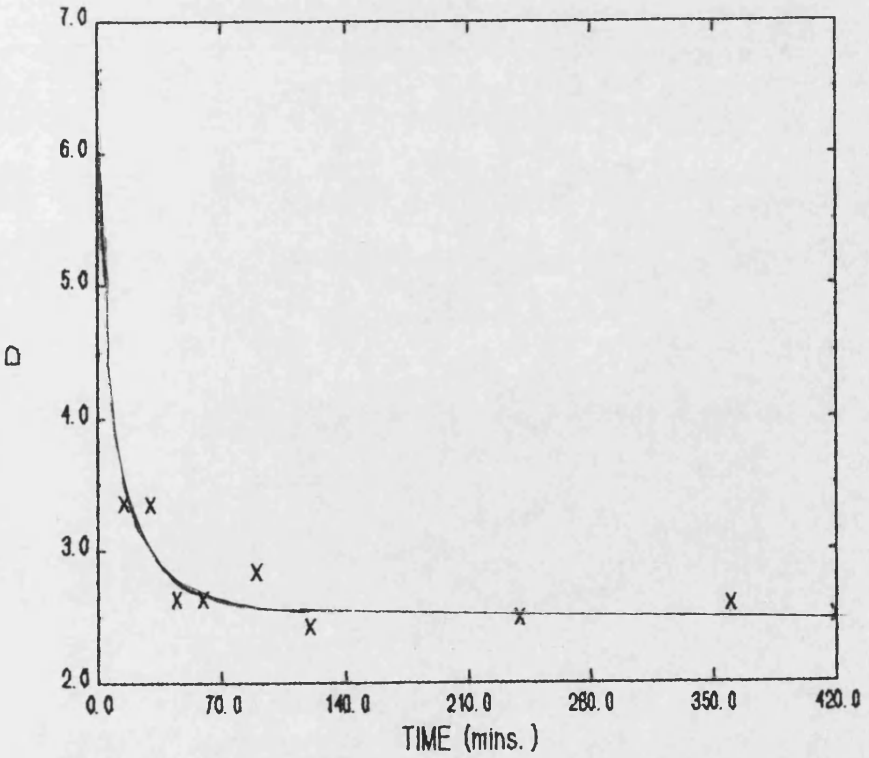


Figure 5.2.3: The effect of sonication upon the molecular weight distribution

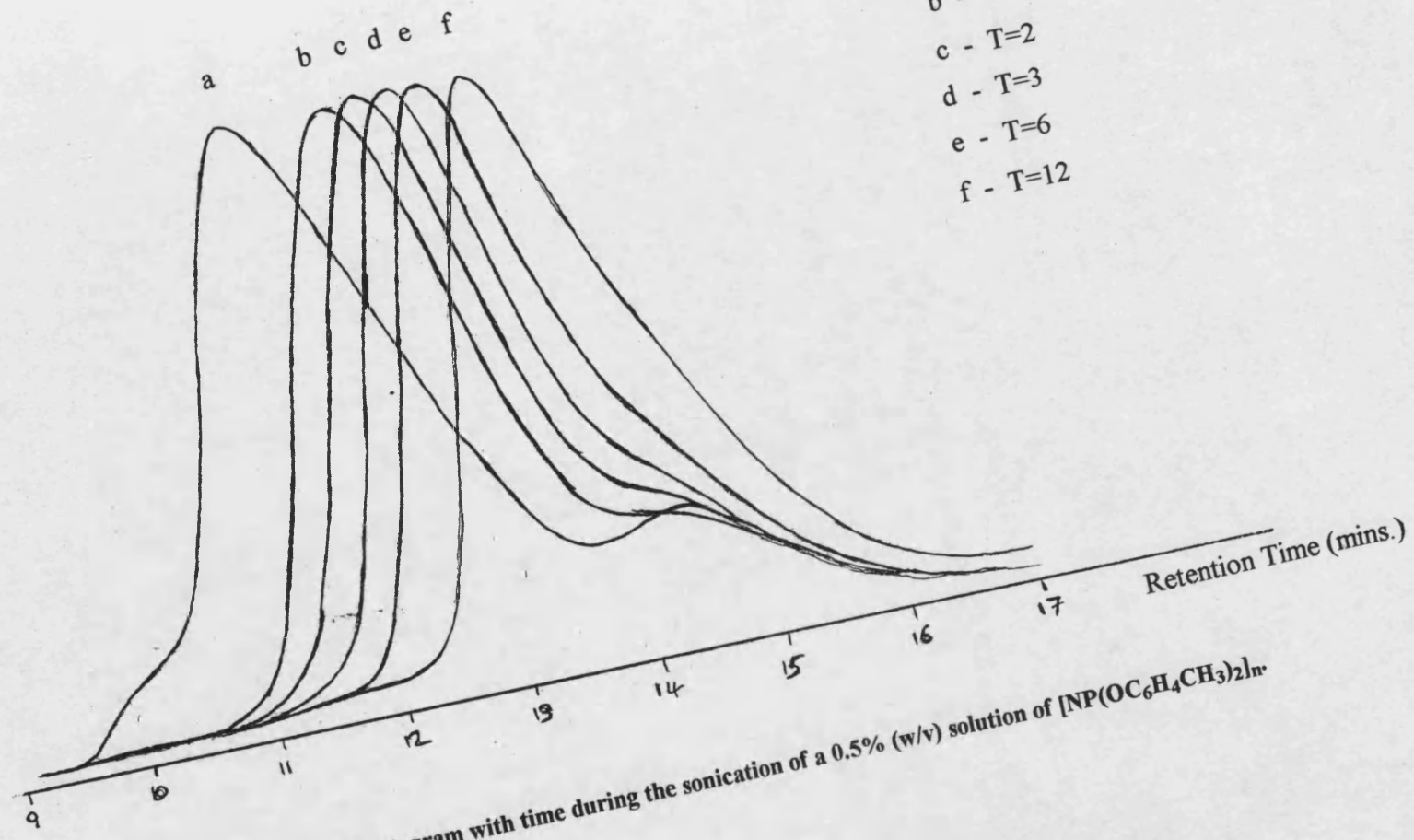


Figure 5.2.4. Variation of the GPC chromatogram with time during the sonication of a 0.5% (w/v) solution of $[NP(OC_6H_4CH_3)_2]_n$.

5.3 ULTRASONIC DEGRADATION RATES.

To be able to quantify the effects of various factors upon the degradation process, it is necessary to be able to define a rate constant for that process. However, the nature of polymer molecules makes the definition of rate equations difficult as the degradation process essentially consists of a series of parallel reactions being performed on a mixture of various chain lengths. The result of this being that an exact treatment would require the consideration of a very large number of rate equations and the solution of a large number of simultaneous equations.

A number of workers have attempted to define a rate equation for the degradation process although to date none of these adequately describes every case. Some of these models have been chosen to be applied to the system studied in this thesis in order to try to characterise the effect of solution concentration and ultrasonic intensity on the degradation.

5.3.1 THE RATE MODELS

1) Schmid rate model[227]

The first attempt at a kinetic model, which has also been one of the most extensively applied to ultrasonic systems, was by Schmid. Based upon experimental observations of the ultrasonic degradation of solutions of polystyrene in toluene, Schmid concluded that the rate of degradation dB/dt (the number of chain breaks per unit time) of a molecule with a degree of polymerisation, P_t, at time t, was proportional to that fraction of the total chain which exceeded the limiting degree of polymerisation, P_{lim}

$$\frac{dB}{dt} = k(P_t - P_{lim}) \qquad \text{where } P_t > P_{lim}$$

where P_t and P_{lim} are the degrees of polymerisation at time t and at the end of the degradation, and k is the rate constant. Schmid found experimentally that the rate constant of degradation depends upon the concentration of the polymer solution and on the chain length of the molecule. Since $P_t = M_t/M_o$ and $P_{lim} = M_{lim}/M_o$, integration leads to

$$\frac{M_{lim}}{M_t} + \ln\left(1 - \frac{M_{lim}}{M_t}\right) = -\frac{k}{c}\left(\frac{M_{lim}}{M_o}\right)^2 t + \frac{M_{lim}}{M_i} + \ln\left(1 - \frac{M_{lim}}{M_i}\right)$$

where M_0, M_i and M_t are the molar masses of the monomer, initially and at time t respectively and c is the solution concentration in base moles dm^{-3} (moles of monomer).

Hence a plot of $-\left[\frac{M_{iim}}{M_t}+\ln\left(1-\frac{M_{iim}}{M_t}\right)\right]$ vs. t should be linear with slope of $\frac{k}{c}\left(\frac{M_{iim}}{M_o}\right)^2$

Despite the main problem of this model being the assumption of an initially monodisperse polymer and that the variation of molar mass distribution during degradation is not considered it has been found to give good linear fits for a range of systems[228] and hence will be considered in this study.

2) El'tsefon and Berlin rate model.

Study of the ultrasonic degradation of polystyrene solutions in benzene lead El'tsefon and Berlin[229] to predict, empirically, that the degradation followed the equation

$$P_t=\frac{P_i}{\sqrt{1+2\beta P_i^2 kt}}$$

where β is a constant which takes into account the polydispersity of the polymer. k could be found from the slope of the straightline obtained when plotting $(P_i/P_t)^2$-1 vs. t. Since this model considers the effect of the initial polydispersity of a polymer sample it provides a possible improvement on the Schmid model.

3) Ovenall rate model

Ovenall et al produced a rate equation for the rate of bond breakage during degradation based upon the experimental results of Henglein[187] who monitored the production of macromolecular radicals (formed by bond cleavage during degradation) by the use of a radical scavenger, 2,2-diphenylpicrylhydrazyl, (DPPH). Ovenall plotted the data for the first 10 minutes of sonication and took into account that as the degree of polymerisation changes at constant weight % concentrations, then the number of molecules involved in the degradation also changes. He found that at lower concentrations

$$\frac{dB}{dt} = k(P_t - P_{lim})n_t$$

and that at higher concentrations

$$\frac{dB}{dt} = k\ln\left(\frac{P_t}{P_{lim}}\right)$$

Since $P_t = M_t/M_o$ and $P_{lim} = M_{lim}/M_o$, then substitution and integration gives

$$\ln\left(\frac{1}{M_{lim}} - \frac{1}{M_t}\right) = \ln\left(\frac{1}{M_{lim}} - \frac{1}{M_i}\right) - k\frac{M_{lim}}{cM_o}t$$

A plot of $Ln(1/M_{lim}-1/M_t)$ vs. t gives a straight line with a slope of $-k/c(M_{lim}/M_o)$.

4) Sato and Nalepa rate model[230]

Results from the ultrasonic degradation of cellulose were applied to a model derived by Jellinek[231] for a random degradation process which gives the relationship between the number average degree of polymerisation, P_t, and time, t, as

$$-\ln\left(1-\frac{1}{P_t}\right) = kt - \ln\left(1-\frac{1}{P_o}\right)$$

When P_n is large this expression can be approximated to

$$\frac{1}{Pt} = \frac{1}{Pi} + kt$$

since $M_n = P_nM_o$ then,

$$\frac{1}{M_t} = \frac{1}{M_i} + k't$$

where M_t and M_i are the number average molar masses of the polymer at time, t, and initially respectively and $k'=k/M_o$, where M_o is the average molar mass of each monomer unit.

5) Initial rate model

As a comparison to the described kinetic models this model considers the change in M_n over the first 30 minutes of the degradation.

5.3.2 THE EFFECT OF ULTRASONIC INTENSITY ON THE RATE OF DEGRADATION.

The effects of sonication at various ultrasonic intensities upon M_n and M_{lim} are shown in figures 5.3.1 and 5.3.2

As would be expected the general trend is that more degradation is observed (i.e. M_{lim} is lower) for higher ultrasonic intensities.

Perhaps unusually, the molar mass distribution appears to fall to a relatively constant value (within experimental error when taking the error of the Gel Permeation Chromatograph to be 5%) irrespective of the ultrasonic intensity used for the sonication. This is shown in Figure 5.3.3.

The various rate models described in Section 5.3.1 were applied to these systems and the plots obtained shown in figures 5.3.4 to 5.3.8.

(For purposes of clarity not all lines have been shown, however, all rate constants obtained from these plots are listed in Table 5.3.1)

It can be seen that none of the models tried provide a perfect fit for the $[NP(OC_6H_4CH_3)_2]_n$ system, however, all except one, the Sato and Nalepa model Figure 5.3.7, fit with reasonable straight lines for the first hour or so of the sonication. The fact that the Sato and Nalepa model is such a poor model provides further evidence that the degradation is a non-random process.

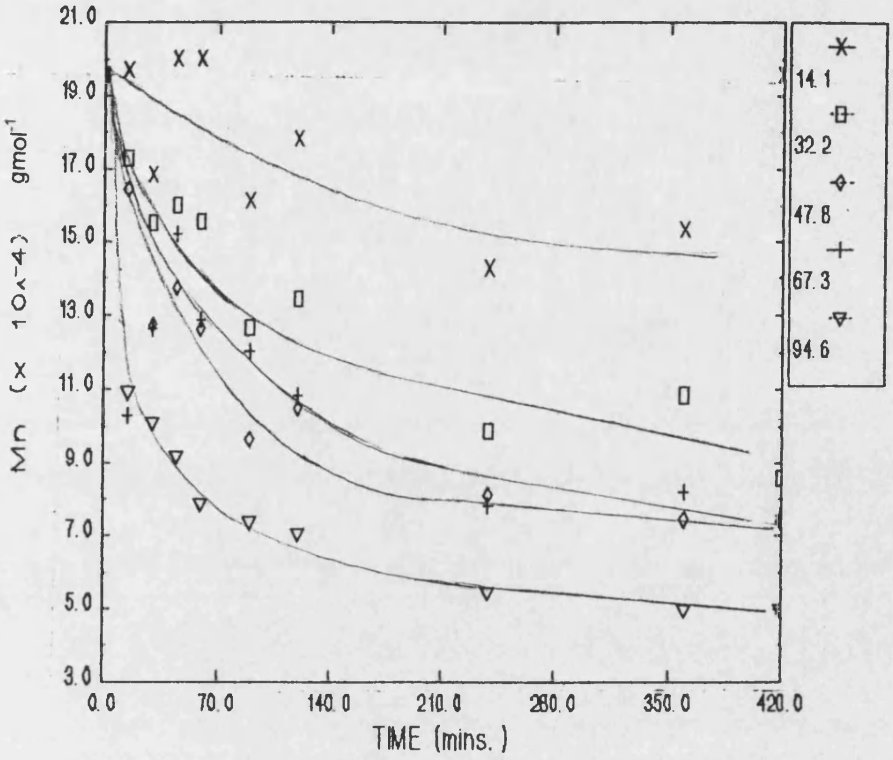


Figure 5.3.1: The effect of sonication at various ultrasonic intensities upon M_n

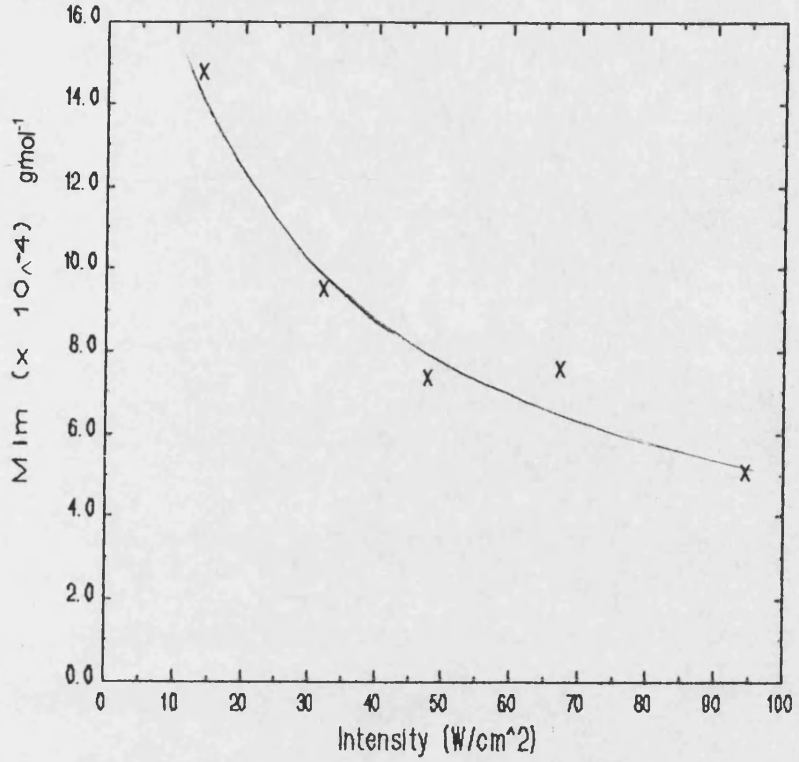


Figure 5.3.2: The effect of sonication at various ultrasonic intensities upon M_{lim}

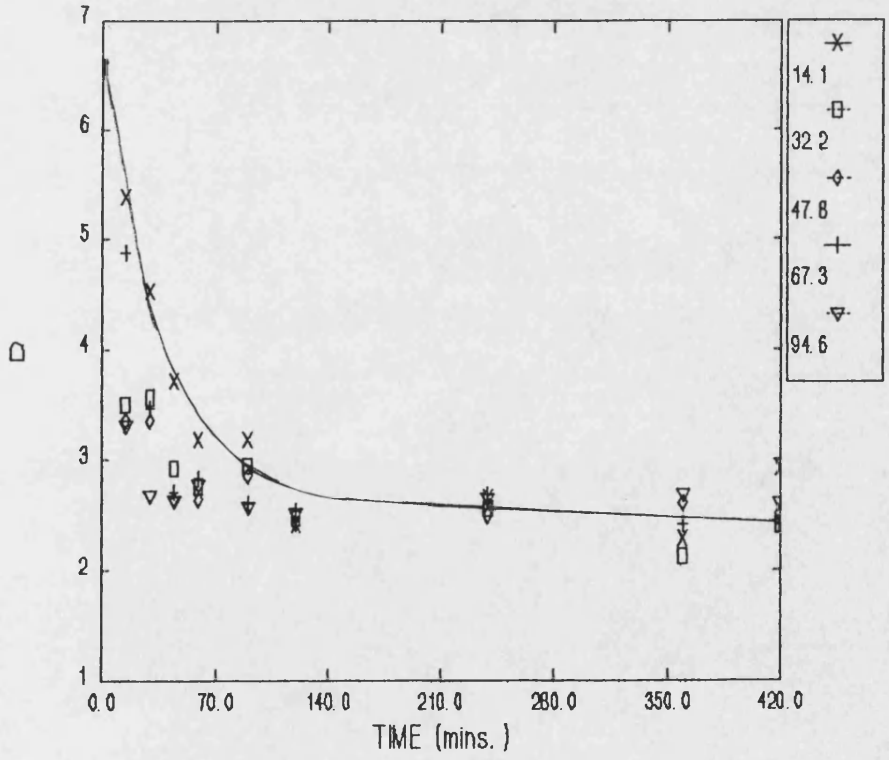


Figure 5.3.3: The effect of sonication at various ultrasonic intensities upon the molecular weight distribution.

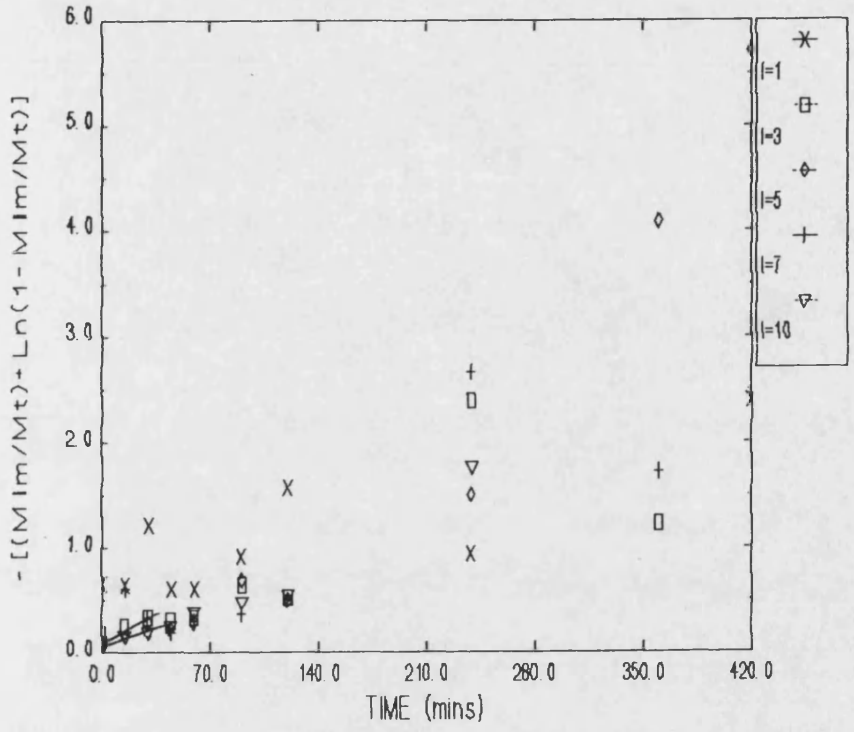


Figure 5.3.4: Application of the Schmid model to the sonication of a polyphosphazene

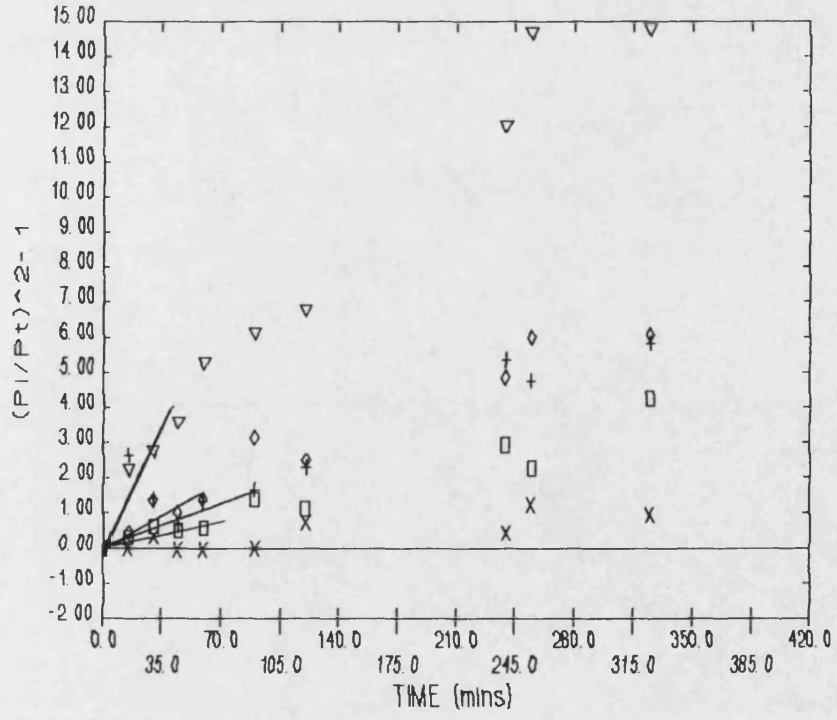


Figure 5.3.5: Application of the Berlin model to the sonication of a polyphosphazene

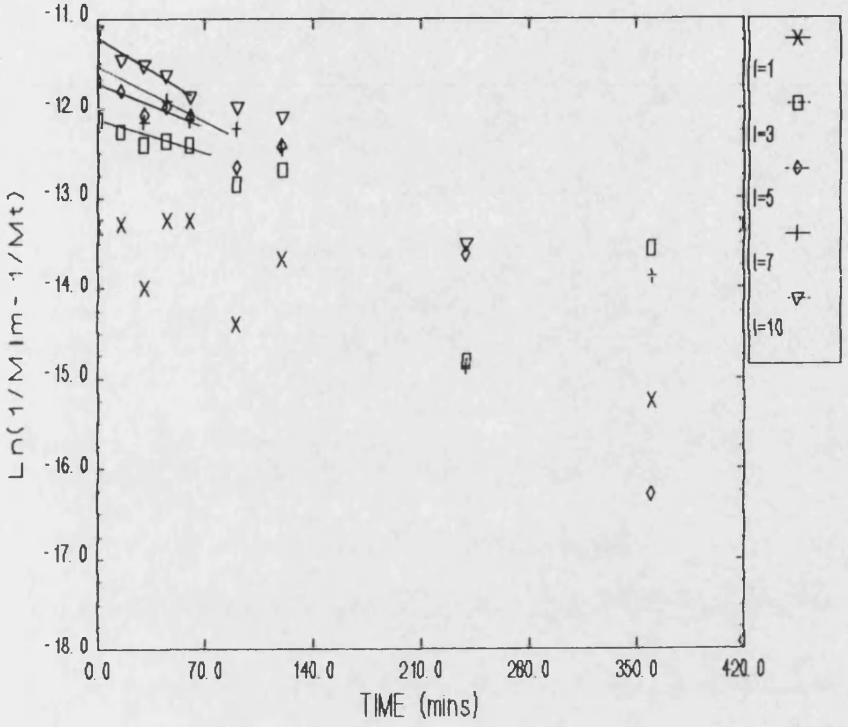


Figure 5.3.6: Application of the Ovenall model to the sonication of a polyphosphazene

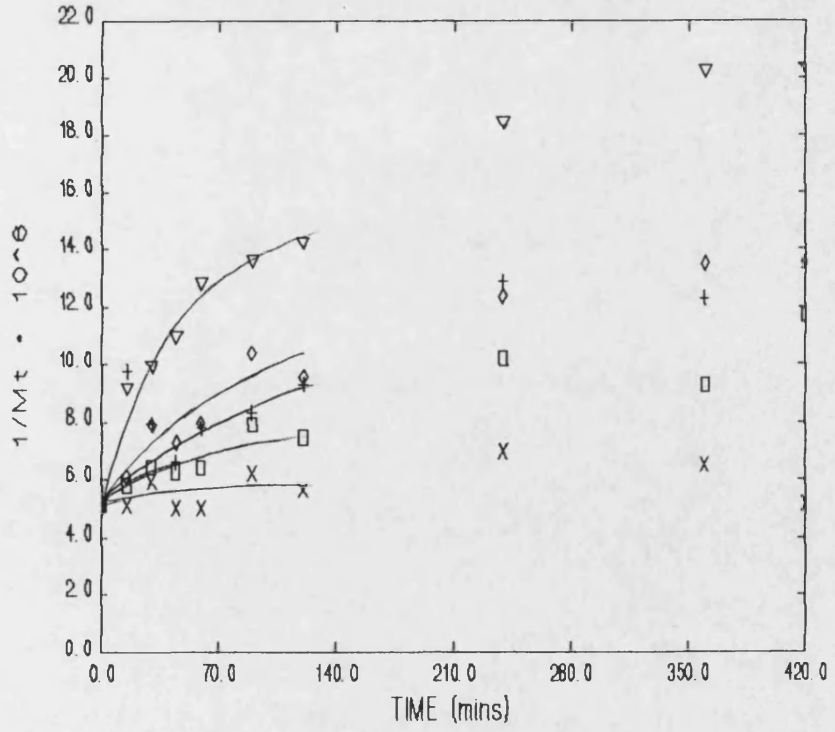


Figure 5.3.7: Application of the Sato and Nalepa model to the sonication of a polyphosphazene

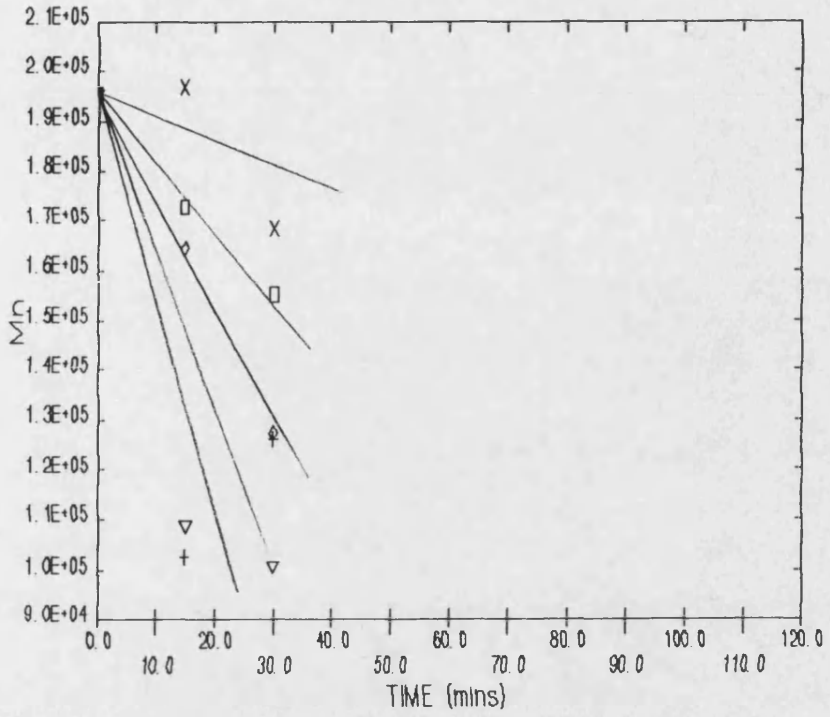


Figure 5.3.8: Application of the Initial rate model to the sonication of a polyphosphazene

Table 5.3.1 Rate constants for the various models

Intensity (Wcm^{-2})	Rate Constants (min^{-1})				
	Schmid ($\times 10^{10}$)	Berlin ($\times 10^{3}$)	Ovenall ($\times 10^{7}$)	Sato and Nalepa	Initial ($\times 10^{-3}$)
14.1	0.0077	-0.81	-0.0414	-	27.0
32.2	0.0355	9.28	0.234	-	40.5
47.8	0.0764	22.78	0.444	-	68.4
67.3	0.0886	4.31	4.066	-	69.4
94.6	0.272	79.53	1.100	-	95.0

Some of the models applied resulted in a negative rate constant, this suggests that these models are unsuitable for describing the degradation under investigation.

The effect of changing the ultrasonic intensity upon the degradation rate constant is shown in Figures 5.3.9 to 5.3.12.

It can be seen that the overall trend is for the rate of degradation to increase as the ultrasonic intensity is increased. This is in agreement with generally accepted ultrasonic theory[144] which says that the radius of the ultrasonic bubble created during cavitation is a function of intensity. As intensity is increased the size of the bubble increases and hence the forces produced upon its collapse are also increased with the result that more effects due to sonication are observed.

5.3.3 THE EFFECT OF CONCENTRATION UPON THE RATE OF DEGRADATION.

The effect on M_n and M_{lim} upon degradation of a sample of $[NP(OC_6H_4CH_3)_2]_n$ at various solution concentrations is shown in Figures 5.3.13 and 5.3.14.

Figure 5.3.13 indicates that sonication has a more pronounced effect on the solutions studied in the order 5% < 1% < 0.1% < 0.5% (w/v). This is clearly in agreement, at the higher concentrations, with the majority of previous work carried out on ultrasonic degradation, which says that as concentration is increased then degradation is decreased, however, it is contradictory at the lower concentrations.

A combination of effects may give rise to these observations. The mechanism of degradation is believed to involve stresses set up by the flow of solvent molecules around much larger macromolecules. At higher concentrations these stresses may be reduced by molecular entanglement.

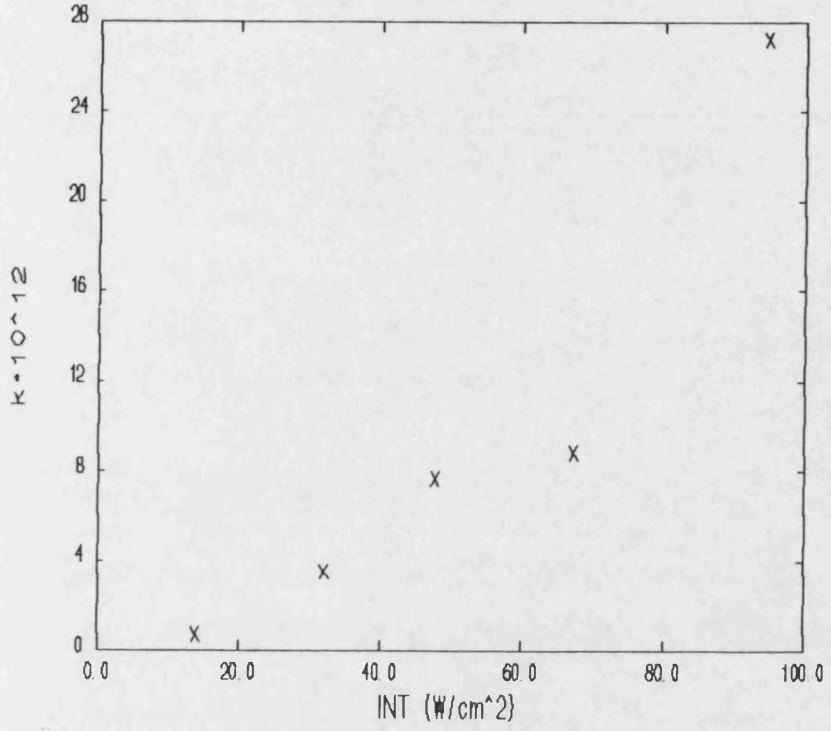


Figure 5.3.9: Effect of ultrasonic intensity on the Schmid rate constant

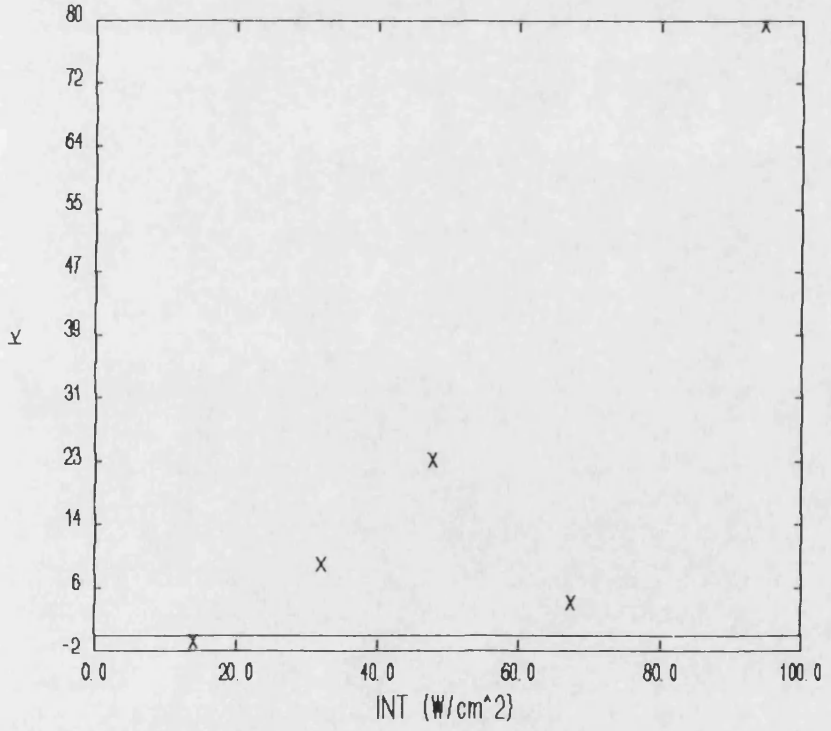


Figure 5.3.10: Effect of ultrasonic intensity on the Berlin rate constant

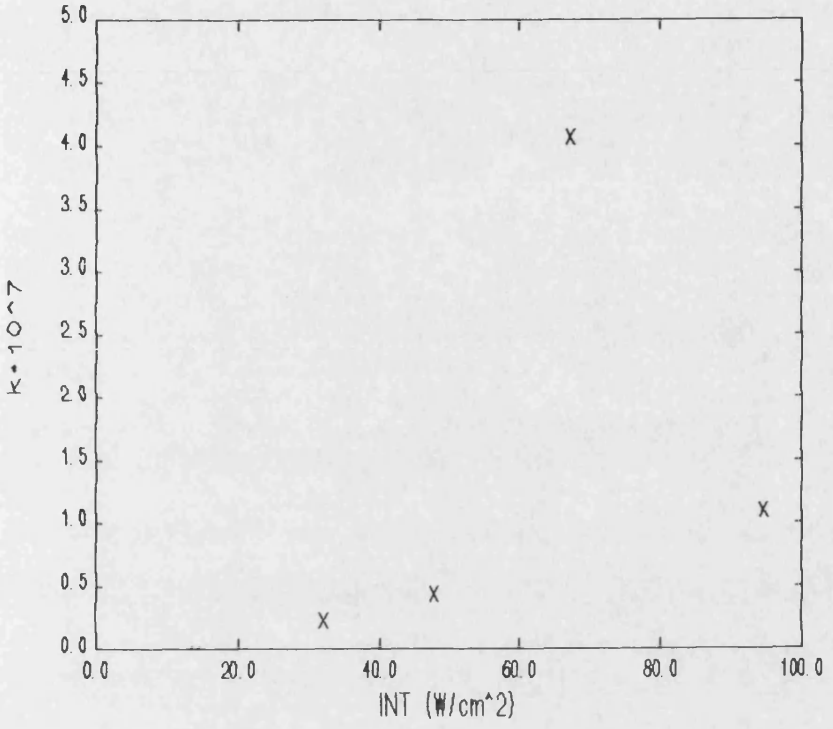


Figure 5.3.11: Effect of ultrasonic intensity on the Ovenall rate constant

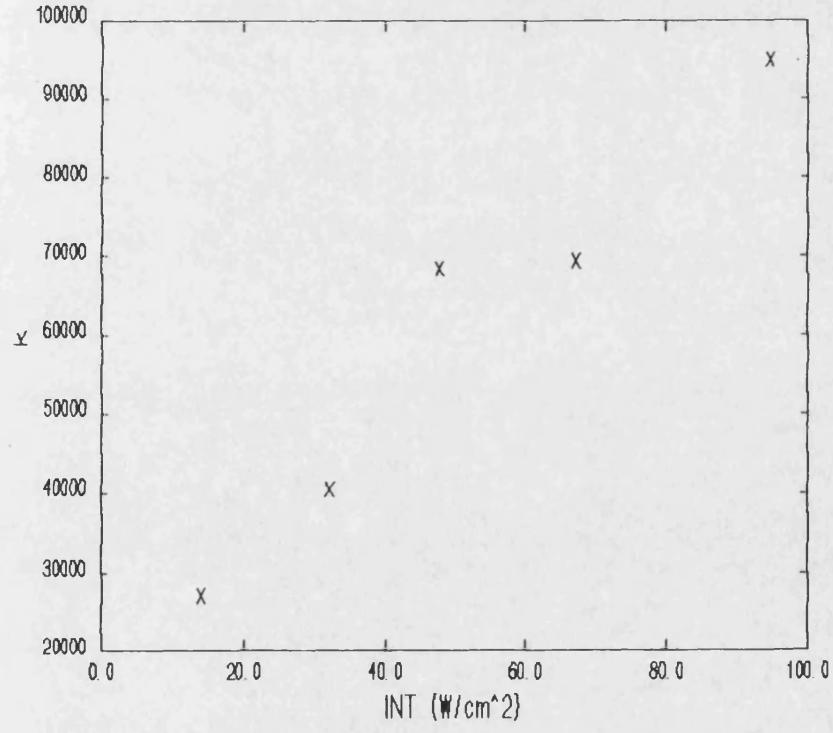


Figure 5.3.12: Effect of ultrasonic intensity on the Initial rate constant

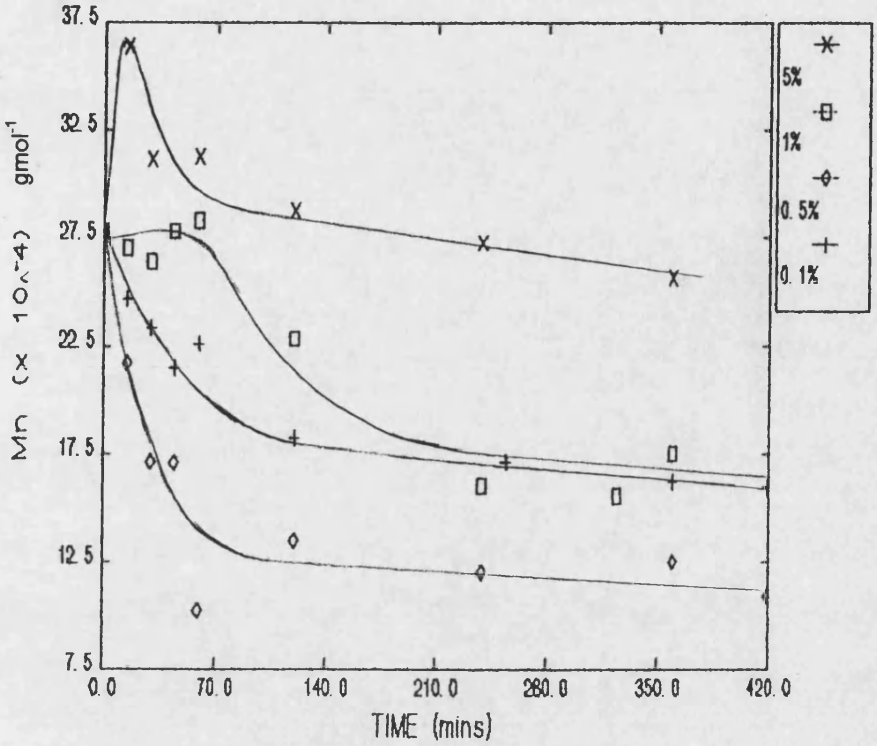


Figure 5.3.13: Effect of solution concentration upon M_n when sonicated

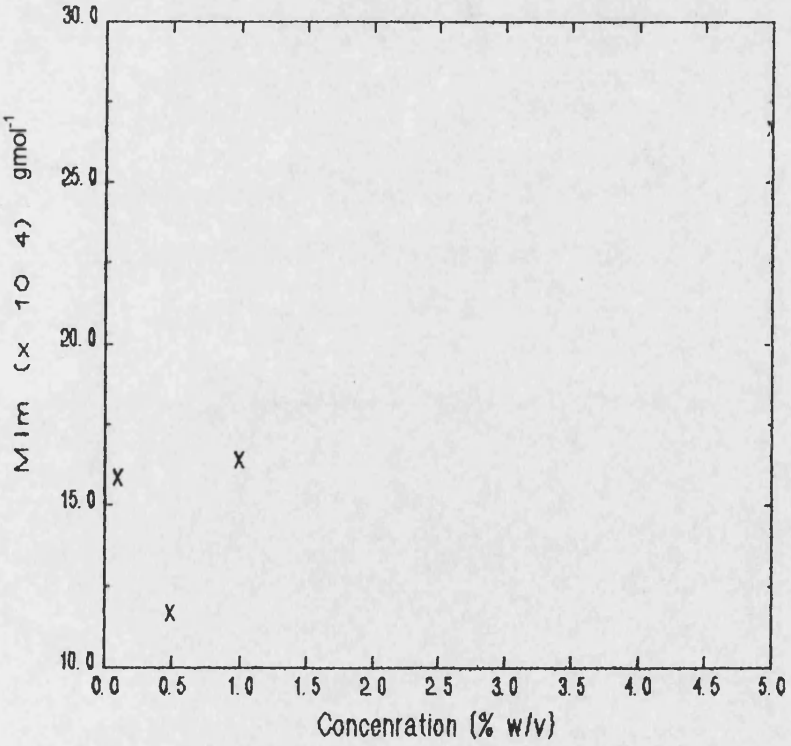


Figure 5.3.14: Effect of solution concentration upon M_{lim} when sonicated

This effect has been shown to limit degradation in polystyrene solutions which are above the critical overlap concentration.[169] It may also be that in higher concentration solutions the 'broken' chains may be close enough to recombine thus reducing the effects of sonication.

At lower concentrations the likelihood that a macromolecule is next to a cavitation bubble upon collapse is reduced in comparison to higher concentrations and so degradation may be suppressed. The viscosity effects mentioned in Section 1.10.4 may also play a part.

The M_n of the 5% (w/v) sample, and indeed the 1% sample to some extent, were observed to rise initially, a phenomenon also observed in the sonication of other systems such as polystyrene[169] and poly(dimethylsiloxane).[232] This is believed to be due to recombination of the polymer fragments, macromolecular radicals in the case of polystyrene, with unbroken polymer chains to form branched macromolecules of a higher molar mass. As in the case of poly(dimethyl siloxane) sonication, it is believed that sonication of $[PN(OC_6H_4Me)_2]_n$ results in heterolytic cleavage and the formation of an ion pair, a theory backed up by some preliminary ESR spectroscopic studies carried out on the sonication of $[PN(OC_6H_4Me)_2]_n$ in which no signal due to radicals could be detected. This provides further evidence for the suggestion that macromolecular ions can attack adjacent chains without causing any further cleavage.[232]

The effect upon the molar mass distributions is shown in Figure 5.3.15.

These observations are unusual and cannot easily be explained, however, it can be seen that an alteration of solution concentration can have a quite substantial effect upon the resulting molar mass distribution of a polymer when being sonicated. Much more so than an alteration of ultrasonic intensity.

The various rate models in section 5.3.1 were applied to the degradations at the different concentrations and the rate constants are given in table 5.3.2.

Table 5.3.2

Concentration (w/v)	Rate Constants (min-1)				
	Schmid ($\times 10^{10}$)	Berlin ($\times 10^{3}$)	Ovenall ($\times 10^{7}$)	Sato and Nalepa	Initial ($\times 10^{-3}$)
5%	0.0328	-0.01	0.7631	-	-33.4[a]
1%	-0.00369	-0.92	-0.01519	-	14.2
0.5%	0.0772	92.3	0.2333	-	10.7
0.1%	0.00481	9.58	0.01708	-	44.7

(a) This value is negative as during the sonication the value of M_n initially rose due to higher molar mass fractions being formed through recombination of macromolecular ions, formed by sonication, with unbroken polymer chains.

Comparison of the rate constants in Table 5.3.2 with those in Table 5.3.1 show a number of inconsistencies. Because of the way that the investigations were carried out it would be expected that several of the rate constants would be the same (for the intensity studies the polymer solutions all had a concentration of 0.5% (w/v), for the concentration studies the solutions were all sonicated at an intensity of 47.8 W/cm^2 thus leading to some overlap in the degradations carried out). This suggests that the rate models used are not appropriate for this particular system. The reason for this may arise from the combined effects of concentration and intensity which were observed during the sonications and which are described in Section 5.4

Plots of the variation of rate constant with solution concentration are shown in Figures 5.3.16 to 5.3.19.

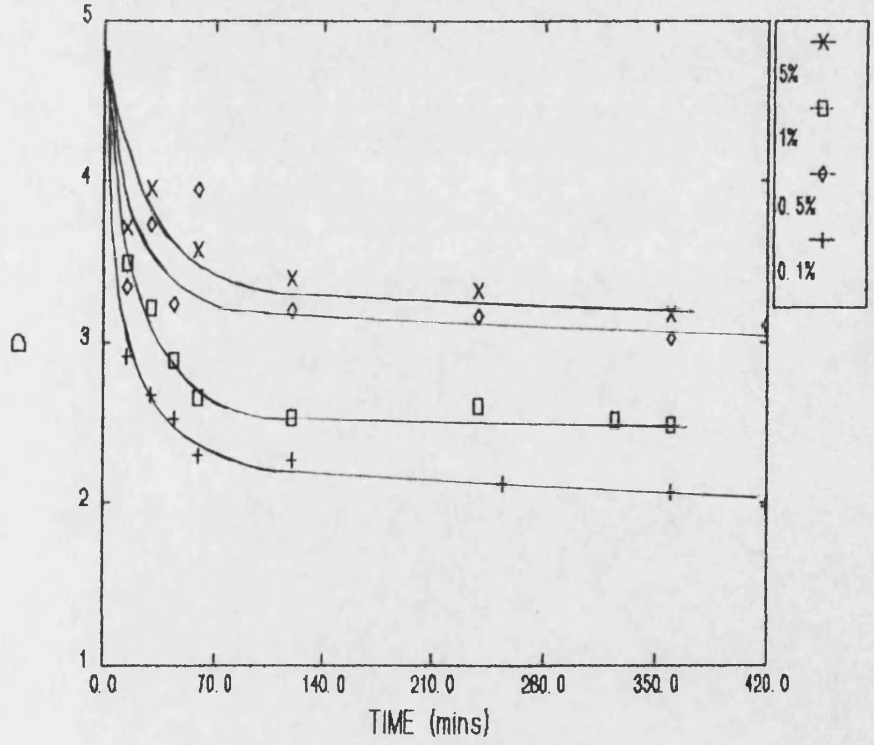


Figure 5.3.15: Effect of solution concentration upon molecular weight distribution when sonicated

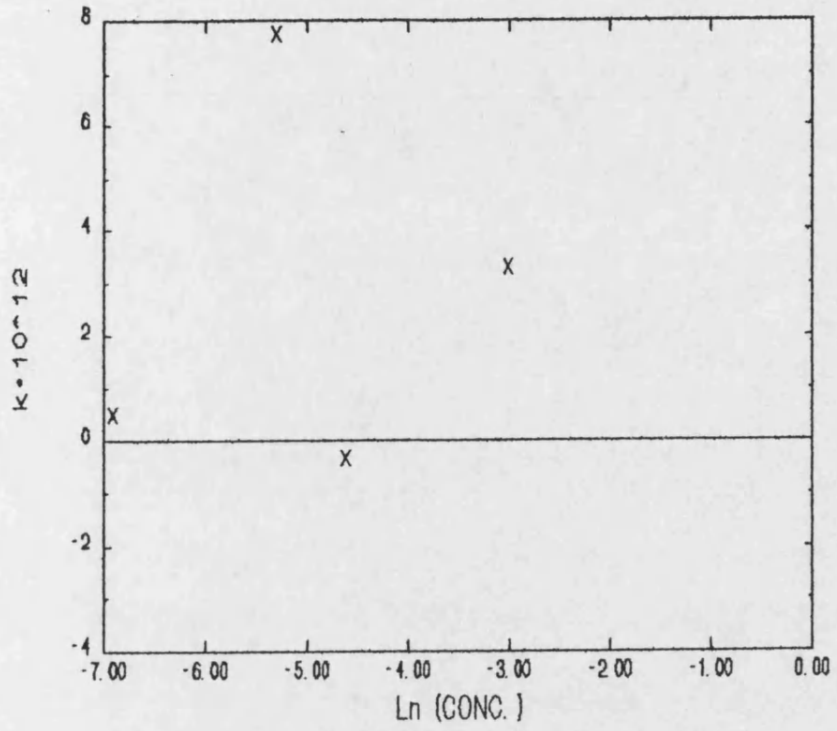


Figure 5.3.16: Effect of solution concentration on the Schmid rate constant

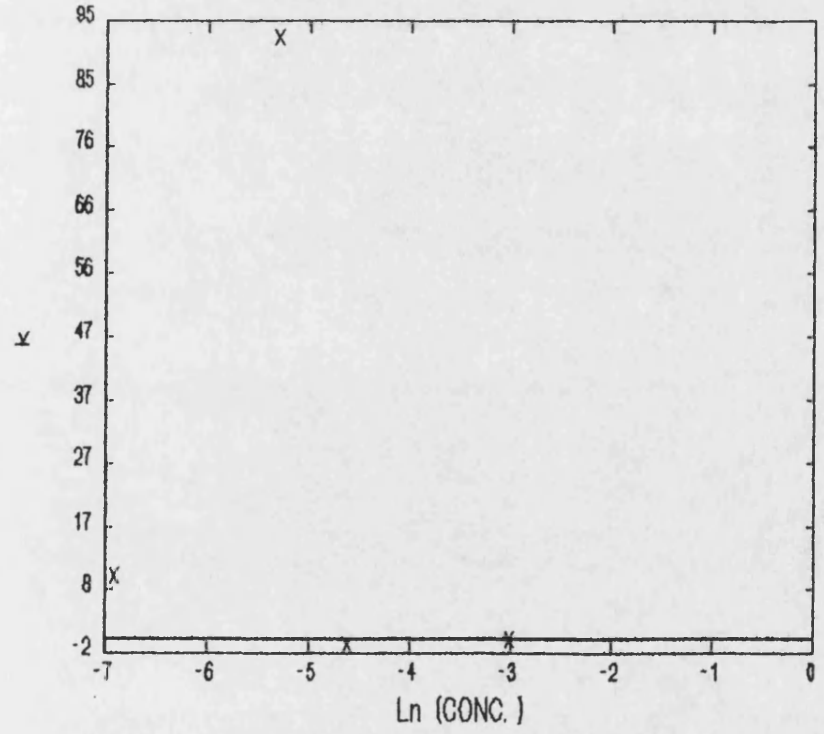


Figure 5.3.17: Effect of solution concentration on the Berlin rate constant

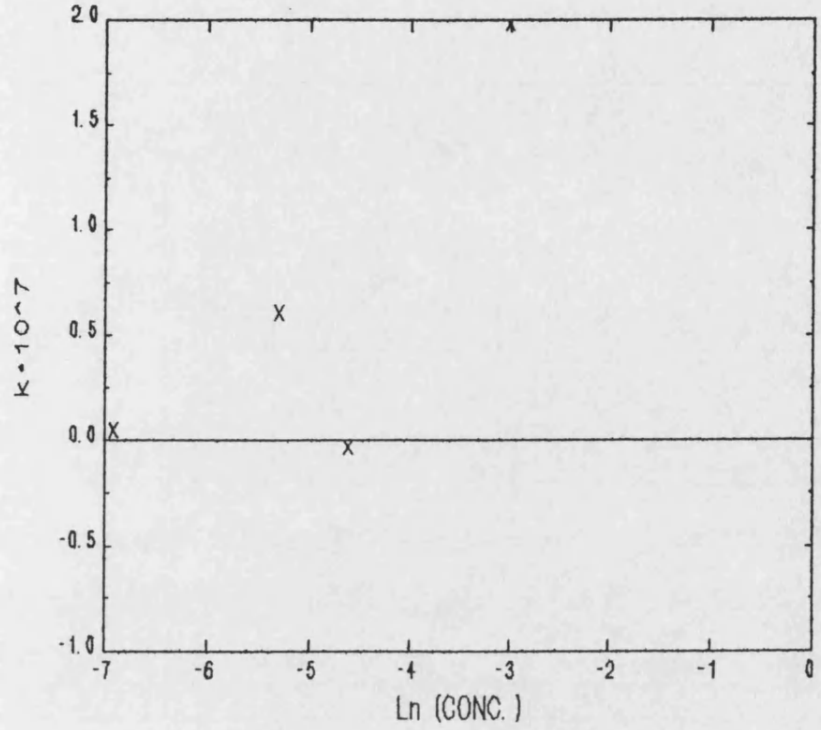


Figure 5.3.18: Effect of solution concentration on the Ovenall rate constant

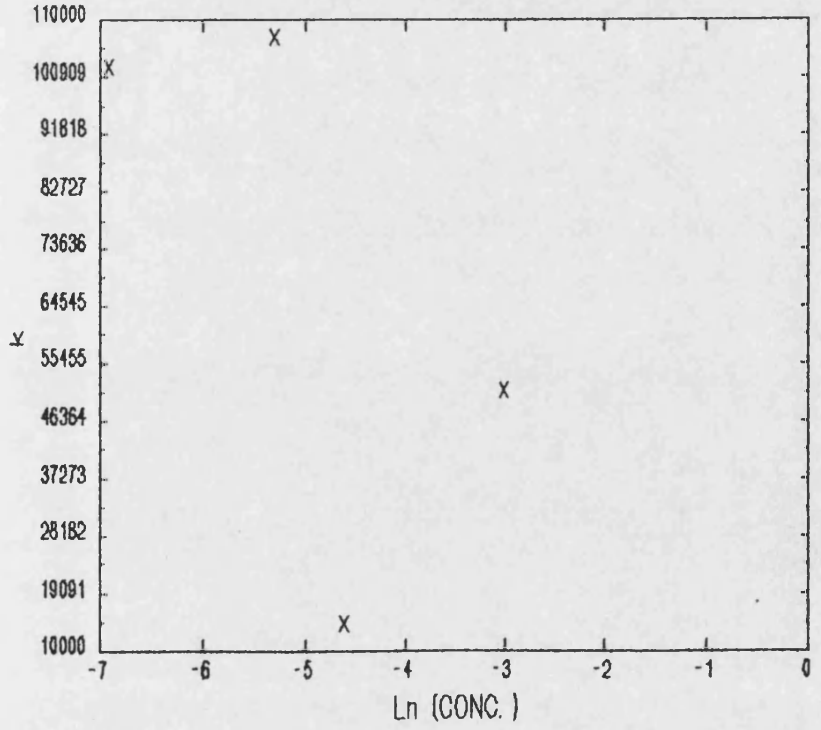


Figure 5.3.19: Effect of solution concentration on the Initial rate constant

As can be seen from these graphs no real correlation between the solution concentration and the degradation rate constant can be found for any of the models tried.

5.4 COMBINED EFFECTS

It was noticed during the studies that varying effects of ultrasonic intensity were observed depending upon the solution concentration. This is demonstrated in Figures 5.4.1 and 5.4.2 which show the effect of sonication upon M_n at intensities of 47.8 Wcm^{-2} and 94.6 Wcm^{-2} for solutions of 0.5% (w/v) and 5% (w/v) respectively.

At the lower concentration the degradations proceed as would be expected with the higher ultrasonic intensity producing the greater effect. At the higher concentration, however, the effect appears to be reversed with the higher intensity resulting in less degradation and a higher M_{lim}. This effect is also seen when the change in polydispersity of the polymer sample is observed. Figures 5.4.3 and 5.4.4.

These observations may be explained by a combination of factors The ultrasonic theory of Noltingk and Neppiras[144] as has already been described suggests that the maximum radius reached by a cavity during its growth is a function of its intensity and that as intensity is increased then the bubble radius increases resulting in greater forces on collapse hence enabling more polymer molecules to be broken. However, if the bubble radius were to increase beyond a certain level then there would be insufficient time between acoustic cycles for collapse to occur. The result would be an effective 'curtain' which would inhibit the passage of further ultrasound and which would lead to a decrease in degradation.

At lower concentrations, and hence lower solution viscosities, this effect is less pronounced, however, at higher concentrations the solution viscosity could be such as to further inhibit the passage of ultrasonic waves and so a point is reached where there is a useful limit, beyond which raising ultrasonic intensity serves only to reduce the amount of degradation observed rather than increasing it as would be expected.

It is clear from the results presented in this chapter that ultrasound can affect pre-formed polyphosphazenes in a quite substantial way, which, from this initial study at least, appear to follow fairly well established trends and theories. It is beyond the scope of this thesis to present a complete study of the various influencing factors on the ultrasonic degradation of polyphosphazenes, however, suggestions as to future work in this area are presented in chapter 7.

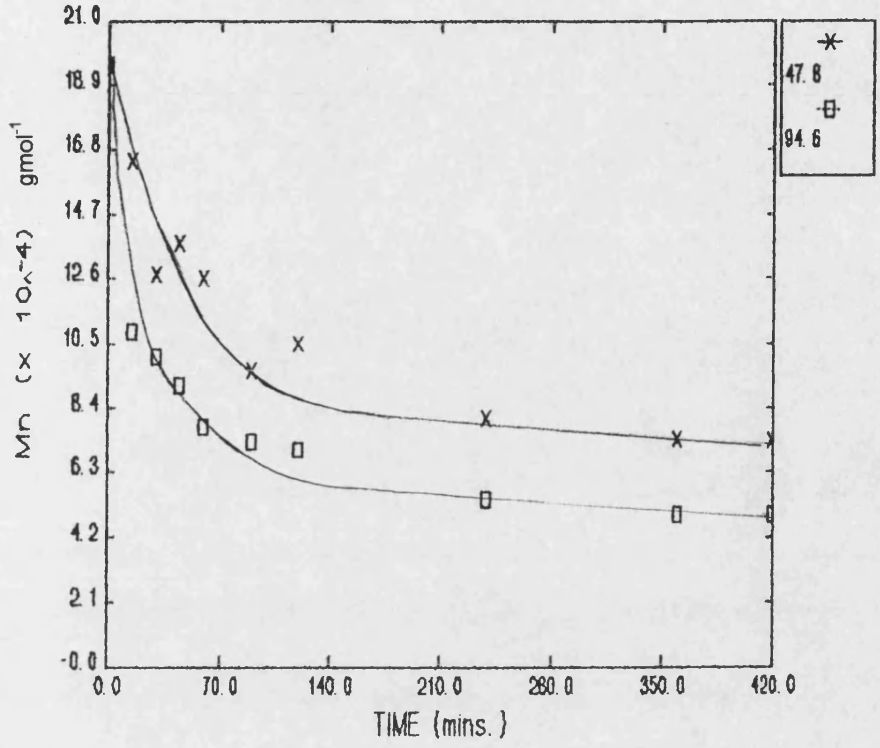


Figure 5.4.1: Effect of varying ultrasonic intensity upon M_n for a 0.5 % (w/v) solution

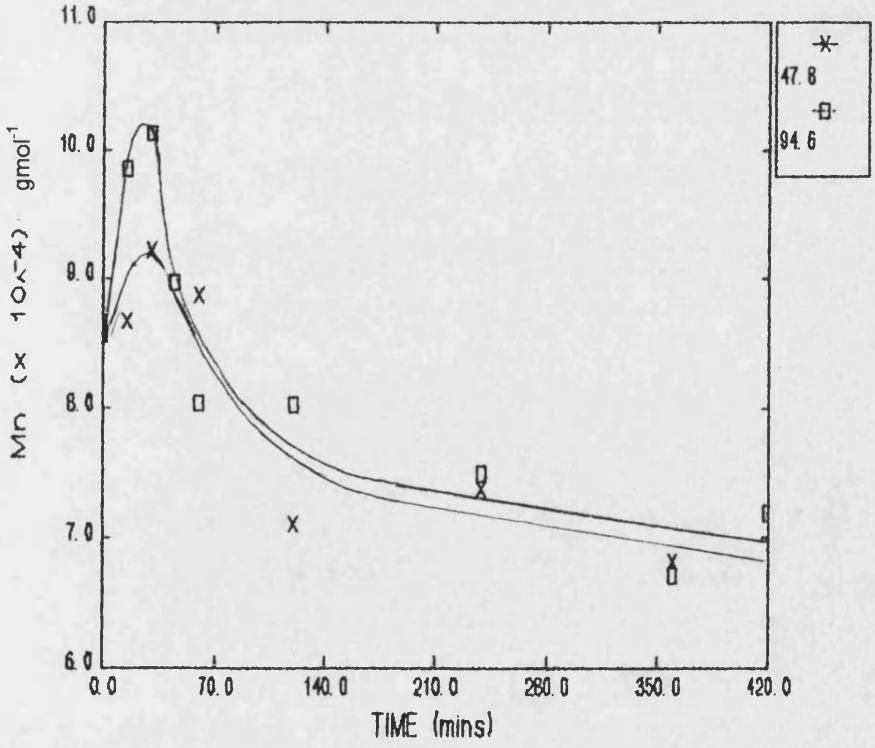


Figure 5.4.2: Effect of varying ultrasonic intensity upon M_n for a 5% (w/v) solution

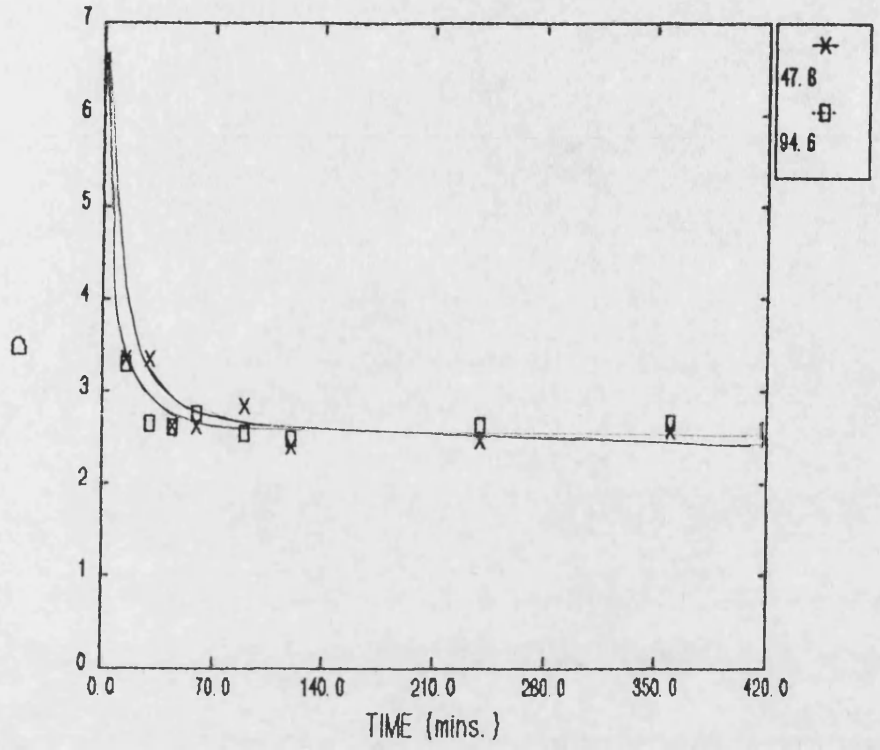


Figure 5.4.3: Effect of varying ultrasonic intensity on the molecular weight distribution for a 0.5% (w/v) solution

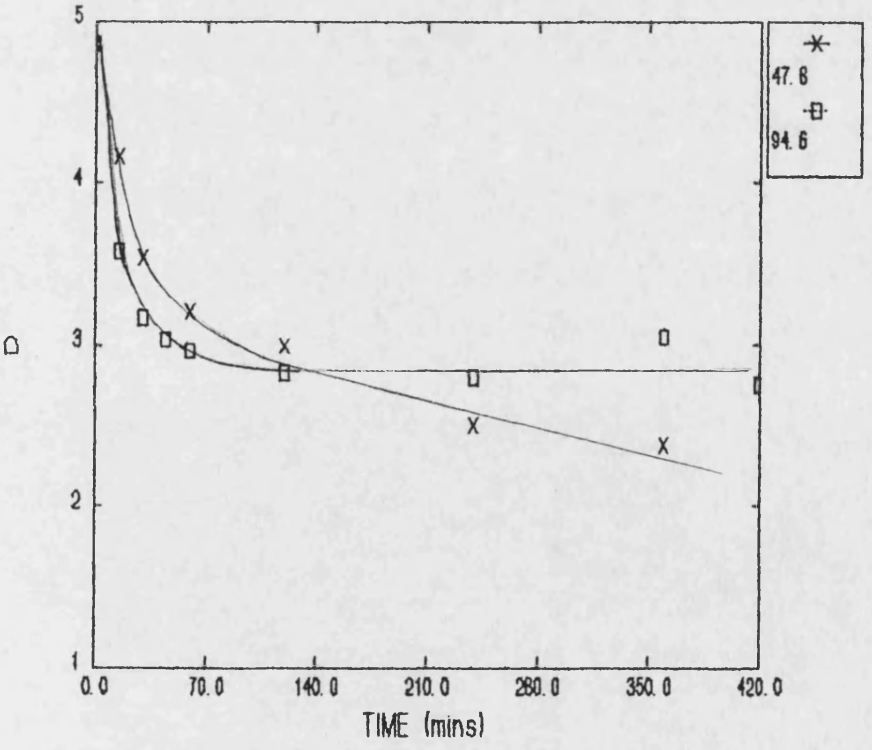


Figure 5.4.4: Effect of varying ultrasonic intensity on the molecular weight distribution for a 5% (w/v) solution

5.5 THE APPLICATION OF ULTRASOUND TO THE SOLUTION POLYMERISATION.

Due to the promising results observed in the application of ultrasound to the pre-formed polyphosphazenes it was decided to investigate whether the synthesis of polyphosphazenes could be aided by ultrasound.

In order to determine whether ultrasound would be useful in the solution polymerisation of $P_3N_3Cl_6$,solutions containing all of the components present in the thermal polymerisation were sonicated at three different temperatures, 25°C, 100°C and 216°C. None of these experiments yielded polymer, the only material isolated being unreacted $P_3N_3Cl_6$. Additional practical problems were encountered at the highest temperature, where, because of the high temperatures involved various transistors within the ultrasonic generator were burnt out. A requirement of the polymerisation reaction is that temperature stability is attained to within a few °C. As the introduction of ultrasound has been shown to raise the temperature of a reaction system (Chapter 4), it was felt that this temperature stability would be difficult to achieve if the polymerisation were to be ultrasonically controlled. It was therefore decided that this method of synthesis of poly(dichlorophosphazene) was not suitable for the application of ultrasound due to the harsh conditions required for the initiation of the polymerisation procedure and the inability of the ultrasonic equipment presently available to operate under those conditions.

A polymerisation method was therefore sought which required much milder conditions. A method based upon the condensation polymerisation of P-trisubstituted-N-silylated phosphinimines reported by Matyjaszewski[113] was chosen. This process was reported to yield substituted polyphosphazenes when monomers were heated to temperatures of approximately 100°C for only a few hours in the presence of an anionic initiator. Some degree of control over the molar mass of the obtained polymer was also reported depending upon the conditions of polymerisation used, Table 5.5.1.

Table 5.5.1.[113]

Polymerisation Temperature (°C)	Observed M_n
95	11000
125	52000
150	100000

It is immediately apparent that these are much less severe conditions than in the solution polymerisation and provided much more practical opportunities to investigate whether ultrasound would be of benefit in the synthesis of polyphosphazenes.

Initially, as a comparison, a 'thermal' polymerisation was carried out which first involved the synthesis of the phosphinimine monomer, $(CF_3CH_2O)_3PNSi(CH_3)_3$, followed by polymerisation at 95°C for 1.5hrs. in the presence of Bu_4NBr initiator. The analytical data recorded for the isolated polymer is given in Table 5.5.2.

The polymerisation was then attempted under the influence of ultrasound (applied via an ultrasonic bath) at room temperature (or more accurately at the temperature to which the ultrasonic bath raised the system, approximately 35°C) for 1.5 hours both with and without Bu_4NBr as initiator. The analytical data for the polymers obtained in these experiments is given in Table 5.5.2. As a follow up to this reaction a conventional polymerisation was carried out at the same temperature, 35°C.

As Table 5.5.2 shows, the structural analytical data for all of the polymers synthesised by this method is essentially the same, implying that the use of ultrasound in this synthesis does not substantially alter the chemical structure of the polymer obtained. It can be seen that all of the reactions gave similar yields apart from that carried out with no initiator present. This implies that initiation is required for this polymerisation to proceed irrespective of whether ultrasound is applied or not.

The differences in the measured values of M_n and γ for the reactions carried out at 35°C show that ultrasound is affecting the polymerisation reaction. This was unexpected as the reaction was carried out in what was believed to be homogeneous solution and is an ionic process[113] - according to the rules of Luche *et al*[213] this means that ultrasound should have no effect on the system. The ultrasonic reaction was observed to yield a polymer with a higher M_n and a lower γ than that produced by the conventional reaction. A lower γ would be expected if degradation was accompanying polymerisation in the system, a process which has been observed in the ultrasonically initiated polymerisation of polystyrene,[217] however, ultrasonic degradation generally results in lower values for M_n, not higher values. Similar results have been observed for the ultrasonic polymerisation of octamethylcyclotetrasiloxane to poly(dimethyl siloxane), PDMS[232] where the explanation given for the higher M_n values was that ultrasound was accelerating the ring-opening polymerisation. This was due to the mixing action of the ultrasound on the heterogeneous polymerisation mixture resulting in the catalyst used being dispersed more evenly throughout the system. A closer look at the phosphazene polymerisation reaction revealed that not all of the Bu_4NBr had dissolved as was first thought, with the result that the system was not completely homogeneous. The application of ultrasound to this mixture would either disperse the

initiator more efficiently throughout the mixture and/or would result in its more efficient dissolution (due to the ultrasound breaking the solid Bu_4NBr into smaller particles, a well known effect[232]). The overall result of this being that initiation would be more homogeneous throughout the reaction mixture leading to a more rapid reaction (giving a higher M_n) and a more even growth of polymer chains (giving a lower γ). If this was the case then a similar effect might be expected upon raising the reaction temperature, and hence the solubility of the Bu_4NBr. This can be clearly seen when the results obtained in the conventional polymerisation reaction carried out at 95°C are compared with those obtained in the 35°C reaction.

Although this first look at the use of ultrasound in the polymerisation of phosphazenes has not been an exhaustive study, there is sufficient promise shown to warrant further investigation, suggestions for which are given in Chapter 7.

Table 5.5.2 : Analytical data for polymers obtained from condensation polymerisation.

Polymer	Yield	NMR Data		GPC Data	DSC	Elemental					
		^{31}P	^{1}H		T_g (°C)	calculated (%)			measured (%)		
						C	H	N	C	H	N
$[NP(OCH_2CF_3)_2]_n$ [a]	0.5g (20%)	-8.45	4.6	$M_n = 53664$ $\gamma = 1.17$	-65.3	21.16	1.78	6.17	19.5	1.80	5.80
$[NP(OCH_2CF_3)_2]_n$ [b]	0.7g (17%)	-8.50	4.6	$M_n = 35671$ $\gamma = 1.47$	-65.8	21.16	1.78	6.17	19.6	1.80	5.85
$[NP(OCH_2CF_3)_2]_n$ [c]	0.23g (18%)	-8.45	4.5	$M_n = 48434$ $\gamma = 1.14$	-66.4	21.16	1.78	6.17	19.65	1.81	5.92
$[NP(OCH_2CF_3)_2]_n$ [d]	0.09g (8%)	-8.54	4.6	insufficient material	-						

(a) Conventionally synthesised polymer (95°C, 1.5hrs. with Bu_4NBr initiator)

(b) Conventionally synthesised polymer (35°C, 1.5hrs. with Bu_4NBr initiator)

(c) Ultrasonically synthesised polymer (35°C, 1.5hrs. with Bu_4NBr initiator)

(d) Ultrasonically synthesised polymer (35°C, 1.5hrs. no Bu_4NBr initiator)

CHAPTER 6

CONCLUSIONS

In this initial study, the effect of ultrasound on a variety of cyclophosphazene substitution reactions has been looked at as well as the potential for the ultrasonic synthesis of polyphosphazenes. In addition the effect of ultrasound on a preformed polyphosphazene has been investigated. It has been found that in general, applications at the polymeric level show more promise than those at the cyclic level.

6.1 : CYCLOPHOSPHAZENE REACTIONS

The conventional substitution reactions of $P_3N_3Cl_6$ have resulted in the observation of some complex reaction systems in which a variety of side reactions have been observed to occur For example, in the reaction of $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol it has been shown that as well as the expected nucleophilic substitution, some bi(cyclophosphazene) formation is also occurring. When DMF was used as the reaction solvent it was found that $P_3N_3Cl_6$ preferentially reacted with this and resulted in the formation of very complex product mixtures.

The reaction of $P_3N_3Cl_6$ with glycidol has been shown to result in not only the expected substitution products but also the further reaction of the epoxide oxygen atom with a phosphazene phosphorus atom. This has been shown to occur in a similar manner to the reaction of 1,3-propanediol with $P_3N_3Cl_6$. In addition, it has been demonstrated that the glycidol in the reaction system can polymerise with the result that the polymeric species can also react with the $P_3N_3Cl_6$.

Application of ultrasound to the nucleophilic substitution reactions of $P_3N_3Cl_6$ with both p-cresol and trifluoroethanol resulted in the observation of higher levels of substitution as well as an increase in the total amount of substituted products. This initially appeared to condradict the "rules" for predicting the effect of ultrasound developed by Luche *et al* as in a homogeneous solution no effect would be expected. It was discovered, however, that the ultrasound resulted in an increase in the reaction temperature and thus a corresponding increase in the amount of nucleophilic substitution occurring in the system.

This phenomenon was also observed in the reaction of $P_3N_3Cl_6$ with glycidol where again an increase in the amount of nucleophilic substitution was found to be occurring upon the application of ultrasound. In this system it was also observed that any side reactions of a similar nature (such as further reaction of the epoxide ring with a phosphazene phosphorus atom or polymerisation of the glycidol followed by reaction with the phosphazene ring as were identified in the conventional reactions) would also be affected in the same way.

As a result of the changes observed in these systems being attributed to a simple rise in reaction temperature they can be proposed as further evidence for the validity of the "rules" developed by Luche *et al.*

In the reaction of $P_3N_3Cl_6$ with Grignard reagents ultrasound was used, again on the basis of Luche's rules, in order to try obtain information concerning the metal-halogen exchange mechanism which leads to the formation of the bi(cyclophosphazene) product. The results obtained in this study were unexpected and show that the formation of the bi(cyclophosphazene) was disrupted by the application of ultrasound rather than being either unaffected or promoted as would have been expected. It has been suggested in this thesis that this is due to the ultrasound affecting the formation of the metallophosphazene intermediate through cleavage / disruption of the N-Mg interaction present in this species. Some suggestions for testing this proposal have been made.

As a result of these observations no firm conclusions can be made concerning the mechanism of the metal-halogen exchange pathway, although the consideration of various other factors, such as the nature of Grignard reagents and information derived from the crystal structure of a similar phosphazene anion, point towards an ionic mechanism.

The potential uses of the application of ultrasound to cyclophosphazene chemistry would appear to be limited, however, it has been shown that if used as model systems for polymeric reactions some use can be found. For example, the supression of the formation of bi(cyclophosphazene) P-P linkages could mean that the use of ultrasound in reactions of $[PN(Cl)_2]_n$ with Grignard reagents will result in significantly less cross-linking reactions and thus a much more useable product.

6.2 : POLYPHOSPHAZENE REACTIONS

Degradation of Preformed polymers.

The ultrasonic degradation of $[NP(OC_6H_4Me)_2]_n$ has been shown to result in the cleavage of only the polyphosphazene backbone. This is the only degradation of a polyphosphazene reported to proceed in this manner (all other reported methods result in the initial breakdown of side groups on the polymer backbone thus resulting in a completely different material). The nature of the fragments obtained upon degradation has not been fully ascertained, however, initial studies would suggest heterolytic fission and the formation of macromolecular ions.

The degradation process has been shown to follow the same general trends as those displayed in other ultrasonic degradations of polymers (such as polystyrene and PDMS). For example it has been found that as the intensity of the ultrasound is increased then degradation also increases (as displayed by an increased lowering of the M_n of the polymer sample and a larger lowering of the mlar mass distribution) and that more degradation is observed in more dilute solutions. Combined effects have been observed where different effects of altering the ultrasonic intensity occur in solutions of different concentrations. This means that it should be possible to find suitable conditions for the production of polyphosphazenes with almost any desired molar mass and molar mass distribution.

It has also been observed that in more concentrated solutions it is possible for the macromolecular ions produced by degradation to recombine with unbroken polymer chains thus resulting in a higher molar mass.

Various kinetic models, developed during studies of the ultrasonic degradations of a variety of other polymer systems, have been applied to the degradation of $[NP(OC_6H_4Me)_2]_n$. It has been concluded that none of these models provide a good description of the polyphosphazene degradation as many inconsistencies were observed in the various applications of the different models. Some expected trends were observed, however, for example it was shown by several of the models that the rate of degradation increased with increasing ultrasonic intensity. It is believed that the problems encountered in the application of these models could be arising because of the combined effects upon the degradation of concentration and ultrasonic intensity described previously.

Synthesis of Polyphosphazenes.

Application of ultrasound to the bulk and solution synthesis of $[NPCl_2]_n$ from $P_3N_3Cl_6$ has been shown to be impractical with currently available equipment.

In the condensation polymerisation of presubstituted polyphosphazenes it has been found that the application of ultrasound results in the formation of polymers with a higher molar mass and lower molar mass distribution than those obtained from the conventional reaction (indeed some of the lowest molar mass distributions reported in the formation of polyphosphazenes have been observed). This was attributed to the more efficient distribution of the slightly insoluble polymerisation initiator throughout the reaction mixture and is in agreement with predictions made based upon "Luche's rules."

The work described in this thesis has been an initial study into the possible applications of ultrasound in phosphazene chemistry. Although it has been found that in many areas ultrasound should indeed be of value it is recognised that more work is required. As such, Chapter 7 describes some suggestions for further work in this area.

CHAPTER 7

SUGGESTIONS FOR FURTHER WORK

Work carried out in this thesis has suggested that ultrasound can have a major role in phosphazene chemistry, for example, at the cyclic level it has been shown that ultrasound has the potential to aid the elucidation of reaction mechanisms. At the polymeric level, where most promise has been displayed, the use of ultrasound has been shown to result in the tailoring of the properties of preformed polyphosphazenes. At the synthetic level, control over the polymer obtained has been shown to be a viable proposition.

Although great promise has been shown this has only been a preliminary investigation into the potential applications of ultrasound to these materials and a great deal further work is required. This I believe is warranted from the results discussed in this thesis and some suggestions for starting points for this further work are outlined below.

7.1 CYCLIC SYSTEMS

The use of rigorously dried DMF as a solvent for the reaction of $P_3N_3Cl_6$ with 2,4,6-tri-t-butylphenol has been shown to considerably simplify the reaction, although the actual products obtained in this reaction were not identified. In order to complete the study begun in this work further investigation along the same lines as has been reported in this work is required in order to elucidate reaction patterns and pathways in this system.

In the reactions with Grignard reagents it is suggested that the use of ultrasound in a system which displays both the nucleophilic substitution and metal-halogen exchange products (such as MeMgCl) would help to confirm whether ultrasound is actually restricting the formation of the bi(cyclophosphazene) product through mechanistic factors. If this was shown to be the case, then the experiments outlined in Chapter 4 should help to shed more light on how this is actually occurring. A greater understanding of the mechanism of this type of reaction would lead to more effective substitution of polydichlorophosphazene with alkyl substituents with less cross-linking restricting the applicability of these reactions.

7.2 POLYMERIC SYSTEMS

7.2.1 Solution polymerisations

Although in the ultrasonic solution polymerisation attempts no actual polymerisation was observed, no conclusive proof was obtained that this would never happen. For this reason a more detailed study should be carried out in which the

temperature at which the ultrasound is introduced is raised gradually until either polymerisation is observed or the ultrasonic probe begins to cut out. If polymerisation is eventually observed then a study of the effect of varying the ultrasonic intensity should be carried out in order to try to quantify any correlations between the properties of the isolated polymer and the polymerisation conditions.

7.2.2 Condensation polymerisations.

Considerable promise was shown by work in this area when the ultrasound was introduced with the use of an ultrasonic bath. However, due to the less controllable nature of this mode of administering ultrasound to a reaction system any further studies in this area should utilise an ultrasonic probe. The use of such an instrument would allow a study of the effect of ultrasonic intensity upon the polymerisation reaction as well as increasing the ease at which other reaction conditions, such as temperature , could be varied. Any such study should try to correlate the polymerisation conditions with the properties of the macromolecular products (such as molar mass distribution etc.) and should also try to find the optimum conditions for obtaining the best yield of product possible.

In the current study only minimal polymerisation was observed when no Bu_4NBr initiator was present, it may well be that at a higher temperature ultrasound alone may be sufficient to initiate the polymerisation process. A study of the effect of temperature and ultrasonic intensity on the uninitiated polymerisation system should be carried out to see if this is a possibility. Also, Matyjaszewski et al[113] report that the amount of initiator added to the polymerisation system affects the molar mass of the polymer obtained. An interesting study would be one in which ultrasound is used in conjunction with this information to possibly further control the properties of the polymer obtained.

A study of the kinetics of ultrasonic polymerisation should reveal if the arguments put forward in this thesis to explain the action of ultrasound on the system were sound by giving an indication of the rate of growth of the polymer chains during the synthesis and of the nature of this growth.

7.3 SONICATION OF PRE-FORMED POLYPHOSPHAZENES.

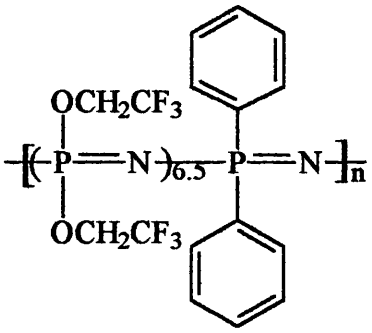
The work carried out in this thesis included the variation of only a few parameters which can affect the outcome of an ultrasonic polymer degradation, any further work should include a study of the effect of those additional factors mentioned in section 1.11.3, i.e temperature, solvent and dissolved gases. A comprehensive study

should also include the effect of the initial molar mass of the polymer upon degradation and also the nature of the polymer itself. For example it is known that unsymmetrically substituted phosphazenes tend to have bonds of unequal length[233,234] and therefore probably of unequal strength and so if unsymmetrically substituted polyphosphazenes were to be sonicated, cleavage of the macromolecule might be observed to be occurring preferentially at one site over another. If this was found to be so then the effect of increasing the electron donating capabilities of polymer side groups, for example, would make an interesting study.

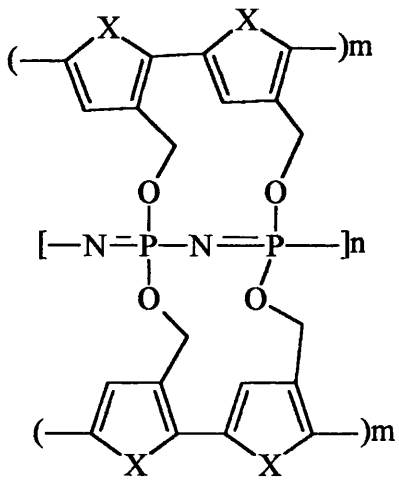
It has been suggested in this thesis that ultrasonic degradation leads predominantly to macromolecular cleavage with the polymer side groups remaining intact. The nature of the cleaved species has not been determined, however, and so a study designed to determine this could be carried out. If macroradicals are formed, such as when polystyrene is sonicated,[169] then these should be detectable by performing the sonication in the presence of a radical trap and by the use of electron spin resonance, ESR, measurements (although preliminary investigations carried out during this work appear to discount this mode of cleavage). If macromolecular ions are formed, such as in the sonication of poly(dimethyl siloxane),[231] and as is strongly suggested by this work, then these may be detectable by sonication in the presence of radioactive labelled species which may be incorporated into the new macromolecular structure.

7.4 OTHER WORK.

Ultrasound has been used in the preparation of various copolymer systems,[216??] if ultrasound could be utilised to prepare copolymer systems containing polyphosphazenes then materials with properties widely different from either of the homopolymers would be accessible. To date the majority of work concerning polyphosphazene copolymers has concentrated on polymers with mixed substituents on the polymer backbone, for example[96] (XLIX), or on polyphosphazenes in which the side groups themselves may also be polymerised.[235] (L)

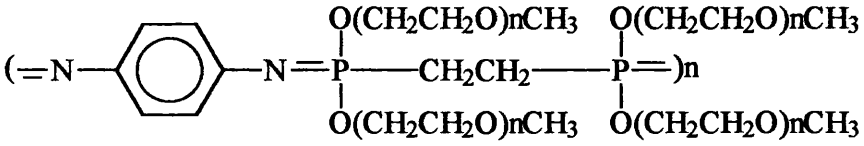


(XLIX)



(L)

Recently, however, copolymers in which the backbone consists of different structural units have been prepared, for example, organo-λ^5-phosphazenes[236] such as (LI)



(LI)

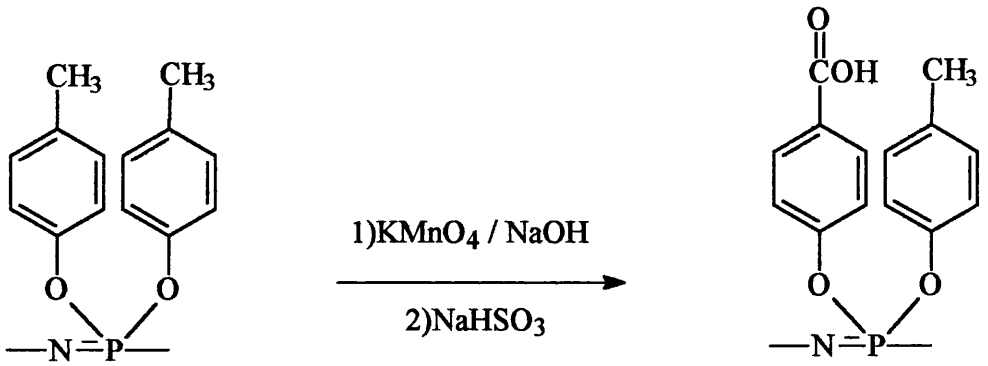
The syntheses for these types of materials are fairly complex and are long processes (often lasting up to 10-12 days) and so any improvement would be welcome. It could be envisaged that, depending upon what type of species is generated upon polyphosphazene degradation, these type of materials may be more easily prepared with the use of ultrasound directly from the polyphosphazenes themselves.

Another example of a multicomponent polymer system is an interpenetrating polymer network, IPN, in which the two polymer components are polymerised and crosslinked in close proximity to each other. IPN's generally have properties which are a hybrid of the properties of their components. A few IPN's exist which consist of polyphosphazenes and organic polymers such as polystyrene and poly(methyl methacrylate).[237]

It is known that ultrasound can initiate polymerisation in styrene and methyl methacrylate[169] and so it would be possible to apply ultrasound to the synthesis of these type of materials.

As was demonstrated in chapter 1 one of the reasons for studying polyphosphazenes is the vast diversity of side groups which can be attached tothe polymer backbone, thus giving a wide range of accessible properties. It has been shown possible to chemically alter the nature of the side groups once attached to the polymer skeleton, thus making accessible polymers which perhaps may be either very difficult or even impossible to synthesise in the conventional manner, for example, the p-cresol side group on polyphosphazene film surfaces can be oxidised to give carboxylic acid groups thus altering the properties of that polymer surface.[238] (Scheme 7.1)

Scheme 7.1



As this is a heterogeneous reaction it is highly likely that the application of ultrasound would result in an increase in the efficiency of the reaction. In other systems it may even be possible to develop new side group reactions, with the application of ultrasound,which at present are not possible.

APPENDIX

^{31}P NMR of PHOSPHAZENES

^{31}P NMR ANALYSIS OF PHOSPHAZENES.

In phosphorus-nitrogen chemistry ^{31}P NMR spectroscopy is a very powerful and important tool, indeed it is the major structural analysis technique employed in the current study. The ^{31}P nucleus can be studied readily due to its 100% natural abundance and its spin of 1/2.

In the study of phosphazenes, the use of ^{31}P NMR allows the identification of both positional and stereoisomers and, with careful interpretation, can yield information on skeletal flexibility and the electronic arrangements within a molecule.

1.0: ^{31}P NMR CHEMICAL SHIFTS.

The ^{31}P chemical shift of a particular group within a phosphazene is very dependent upon and sensitive to a number of factors, e.g. molecular environment, and tends to exist as a broad range which can have considerable overlap with the chemical shift ranges of other groups.. This is illustrated by the data in Table 1.

Table 1: Some ^{31}P NMR chemical shift ranges in phosphazenes.[17]

Unit	^{31}P chemical shift (ppm)	reference
PCl_2 (trimers)	14 to 23	14, 192
PCl_2 (tetramer)	-7.4	30
PClPh	29 to 33	240
PPh_2	14 to 30	241, 242
PCl(OAlkyl)	13 to 17	192
$P(OAlkyl)_2$ trimer	15 to 22	14
$P(OAlkyl)_2$ polymer	-3 to -8	14
$P(OAryl)_2$ trimer	9 to 12	14, 243
$P(OAryl)_2$ polymer	-19	14

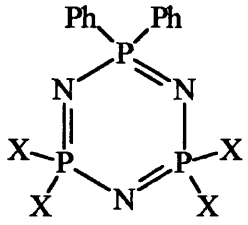
It is clear from this data that ^{31}P chemical shifts cannot, or can only very seldomly, be used for "fingerprint" identification purposes.

Various influences on the value of the chemical shift of a group can be imagined, for example the effects of different ligands. Ligands with different electronegativities would be expected to alter the chemical shifts by changing the electron density within a N_3P_3 ring to varying extents. The introduction of electron withdrawing substituents, for example, might be expected to lead to a contraction of the phosphorus dπ orbitals which in turn would increase the strength of the π-bonding system by enhancing the delocalisation of the lone pairs on the ring nitrogen atoms. As

this would lead to increased electron density at the substituted phosphorus, its chemical shift would be expected to move upfield, relative to its PCl_2 starting point, due to shielding.

The other ring phosphorus atoms, provided their ligands haven't changed, would be expected to now have a slightly +ve environment relative to their environment prior to the addition of the electron withdrawing group. This would have the effect of deshielding the phosphorus nucleus and would lead to a move downfield.

This latter effect is displayed quite well in a series of monosubstituted chlorophosphazenes in which increasing the electronegativity of the substituent does actually lead to a downfield shift in most cases.[192] Also in (1) the PPh_2 shift has been observed to vary depending upon the distribution and nature of the other groups in the molecule.[241, 244]



(1)

The shielding effects expected upon substitution of a particular phosphorus, however, aren't observed nearly as well and it has been suggested that other effects, such as interactions within the R-P-R framework, i.e. steric factors, and the effect of the ligands on the other ring phosphorus atoms could be enough to overide any trends which might be expected.

Various trends have been noted for the behaviour of chemical shifts when compared to the level of substitution within a phosphazene.[245, 45] For example, with aryloxy and alkoxy derivatives the following has emerged.

a) Increasing substitution on a phosphorus leads to upfield shifts.

$$\delta\underline{P}Cl_2 > \delta\underline{P}Cl(OR) > \delta\underline{P}(OR)_2$$

b) Increasing the substitution on a phosphorus atom other than that being observed leads to downfield shifts.

$$\delta\underline{P}NPCl_2 < \delta\underline{P}NPCl(OR) < \delta\underline{P}NP(OR)_2$$

2.0 SPIN - SPIN COUPLING

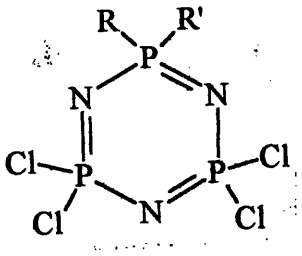
The ^{31}P nucleus, with its spin of 1/2, can couple readily with other ^{31}P, ^{1}H and ^{19}F nuclei (all of which also have spin 1/2), so readily in fact, that ^{31}P NMR spectra are generally proton decoupled in order to simplify the spectra obtained (and also to increase the ease of collection of those spectra.)

Phosphorus - Phosphorus coupling.

Short range coupling between the phosphorus atoms in the ring is readily observed and can give rise to various patterns/types of spectra The expected spectral types for the series of substituted cyclic trimers are given below in Table 3.

More complicated patterns are predicted for more complex molecules, such as an $A_2MM'A'_2$ pattern for symmetrical bi(cyclophosphazenes), this is due to long range, 3 bond coupling which splits the usual 2 bond coupling even further. In practice, however, these patterns are usually "deceptively simple" due to overlap of some of the signals.[199]

Observed coupling constants are dependent upon the substituents bonded to phosphorus, for example, in (2) J_{P1P2} terms generally show higher values as the electronegativities of the substituents R and R' increase.[192] (Table 2)



(2)

Table 2

R	R'	J_{P1P2}
Cl	NMe_2	49.7
Cl	F	78.3
F	F	100

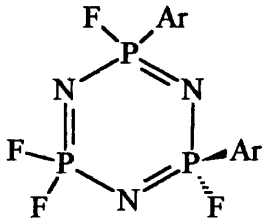
Spin - Spin coupling to other nuclei.

More complicated splitting patterns can be observed when the phosphorus nuclei couple with nuclei in the side groups, such as hydrogen, carbon or fluorine. Coupling with such nuclei can lead to hyperfine splitting of expected spectral patterns in the ^{31}P NMR.[17]

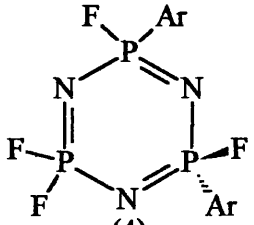
Virtual coupling, splittings due to magnetic interactions involving nuclei with which the coupling constant is zero, is observed in some aryloxy phosphazenes where the phosphorus atom is observed to couple with a carbon atom in the ligand through

the aryloxy oxygen unit.[245] This is more easily observed in ^{13}C NMR due to the relative abundances of the two nuclei. That is in the ^{31}P NMR spectrum, due to a phosphorus nucleus coupling with only 1% of the carbon nuclei present, the peaks appear as very small satellite signals whereas in the ^{13}C NMR spectrum, the ^{13}C nucleus coupling with 100% abundant ^{31}P results in large signals and more easily observed splitting.

Coupling with other, NMR active nuclei can yield valuable structural information, For example, stereoisomers have been distinguished from one another in the diarylfluorophosphazenes (3 and 4) through observations of the effect of the phosphorus - fluorine coupling.[246, 63]



(3)

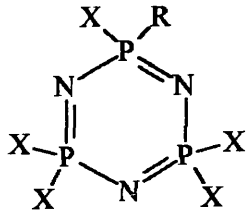
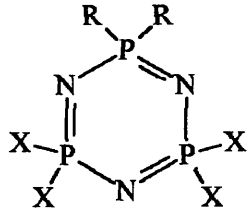
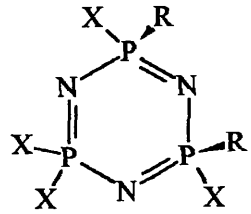
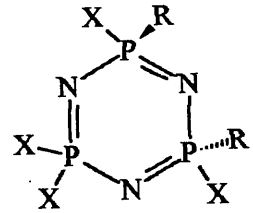
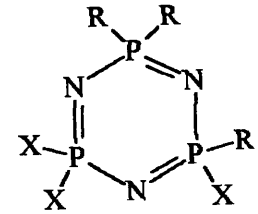
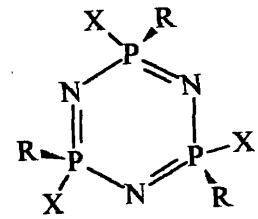


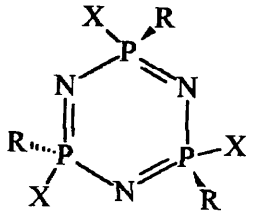
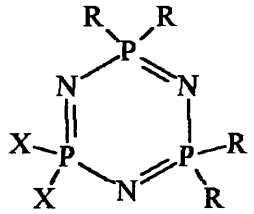
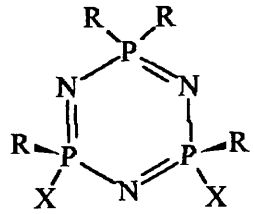
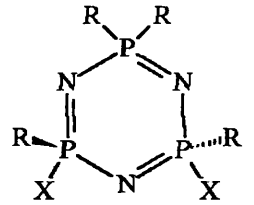
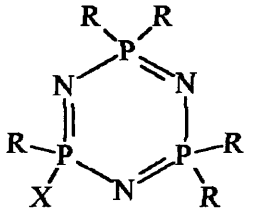
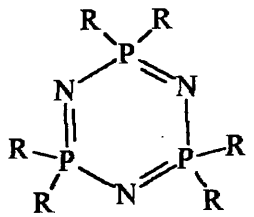
(4)

Phosphorus - hydrogen coupling constants have been obtained by observation of the phosphorus undecoupled proton spectra of hydridophosphazenes[78] whilst signal assignment in propynylphosphazenes was aided by studying the change in splitting caused by phosphorus - hydrogen coupling when a spectrum was run as proton undecoupled.[216]

Other techniques, common in NMR experiments with other nuclei, have also been applied in ^{31}P NMR, for example, 2D COSY ^{31}P NMR has been used to aid in interpretation of the structure of vinyloxyphosphazenes.[57]

Table 3: Expected spectral types for substituted phosphazene trimers.

	PX_2	PX(R)	$P(R)_2$	Spectral type [a]
	doublet	triplet		A_2M
	doublet		triplet	A_2X
	triplet	doublet		AM_2
	triplet	doublet		$A'M'_2$ [b]
	doublet of doublets	doublet of doublets	doublet of doublets	AMX
		singlet		M_3

	PX_2	PX(R)	$P(R)_2$	Spectral type [a]
		doublet and triplet		$M'M''_2$ [c]
	triplet		doublet	AX_2
		doublet	triplet	M_2X
		doublet	triplet	M'_2X' [b]
		triplet	doublet	MX_2
			singlet	X_3

(a) The AMX notation is that which is commonly in use,[247]

- i) For nuclei which have chemical shifts close to each other letters are chosen which are close to each other in the alphabet. For those which have chemical shifts far apart, letters are chosen from opposite ends of the alphabet. Similarly, intermediate chemical shifts result in intermediate letters.
- ii) Several magnetically equivalent nuclei are denoted by subscripts.
- ii) Chemical, but not magnetic, equivalence is denoted by repeating the letter with a prime.

In the table PX_2 is A, PX(R) is M and $P(R)_2$ is X.

(b) The PX(R) groups, in both the bisubstituted and tetrasubstituted non-geminal compounds, are intramolecularly magnetically equivalent. However, the cis PX(R) groups are not magnetically equivalent to the trans PX(R) groups and hence a slight change in chemical shift occurs and two spectra are seen, one for each of the isomers.

(c) In the cis isomer of the trisubstituted compound all of the PX(R) groups are both chemically and magnetically equivalent, hence M_3. In the trans isomer all of the PX(R) groups are chemically equivalent but two of the groups are magnetically different to the third. Again, the groups in the trans isomer are chemically equvalent but magnetically non-equivalent to those in the cis isomer, hence $M'M''_2$.
The overall result of this, in practice, is a signal which consists of overlapping singlet, doublet and triplet all with very similar chemical shifts as is demonstrated by the p-cresol system. (Figure 3.1.1)

REFERENCES

1) R.J. Young, P.A. Lovell, 'Introduction to Polymers' 2nd Edtn. Chapman and Hall, (1991)

2) J.C. Moore, *J. Polym. Sci.*, A2, 835, (1964)

3) J.V. Dawkins, 'Steric Exclusion in Liquid Chromatography of Polymers' Ed. J. Janca, New York, (1984)

4) Z. Grubisic, P. Rempp, H. Benoit, *J. Polym. Sci., Polym. Lett. Ed.*, 5, 753, (1967)

5) H.R. Penton, *ACS Symposium Series 360*, 277, (1987)

6) J. Liebig, *Ann. Chem.*, 11, 139, (1834)

7) H. Rose, *Ann. Chem.*, 11, 131, (1834)

8) J.H. Gladstone, J.D. Holmes, *J. Chem. Soc.*, 17, 225, (1864); H.N. Stokes, *Am. Chem. J.*, 19, 782, (1897)

9) H.R. Allcock, R.L. Kugel, *Inorg. Chem.*, 5, 1016, (1966)

10) H.N. Stokes, *Am. Chem. J.*, 20, 740, (1898)

11) H.R. Allcock, *'Phosphorus Nitrogen Compounds'*, Academic Press, New York, (1972), Chapter 7

12) Reference 11, Chapter 6

13) Reference 11, Chapter 8

14) H.R. Allcock, R.L. Kugel, K.J. Valan, *Inorg. Chem.*, 5, 1709, (1966)

15) H.R. Allcock, J.L. Desorcie, G.H. Riding, *Polyhedron*, 6(2), 119, (1987)

16) Reference 11, Chapter 2; C.W. Allen, *Coord. Chem. Rev.*, 130, 137, (1994)

17) Reference 11, Chapter 3

18) S.K. Ray, R.A. Shaw, *Chem. Ind. (London)*, 1173, (1961); D. Feakins, S.N. Nabi, R.A. Shaw, P. Watson, *J. Chem. Soc., A*, 10, (1968)

19) H.R. Allcock, *J. Am. Chem. Soc.*, 86, 2591, (1964); H.J. Krause, *Z. Elektrochem.*, 59, 1004, (1955)

20) H.R. Allcock, W.J. Birdsall, *Inorg. Chem.*, 10, (1971)

21) P.J. Wheatley, *J. Chem. Soc.*, 2206, (1964)

22) L.S. Bartell, K.W. Hansen, *Inorg. Chem.*, 4, 1777, (1965)

23) P.J. Wheatley, *J. Chem. Soc.*, 5785, (1965)

24) K.A.R. Mitchell, *Chem. Rev.*, 69, 157, (1969)

25) E.A.L. Lucken in *'Structure and Bonding'* (P.Hemmerick et al. Eds.), Springer-Verlag, Berlin and New York, (1969)

26) D.P. Craig, N.L. Paddock, *Nature*, 181, 1052, (1958); D.P. Craig et al., *Chem. Soc.*, 1376, (1961); D.P. Craig, K.A.R. Mitchell, *J. Chem. Soc.*, 4682, (1965); D.P. Craig, N.L. Paddock, *J. Chem. Soc.*, 4118, (1962)

27) M.J.S. Dewar, E.A.C. Lucken, M.A. Whitehead, *J. Chem. Soc.*, 2423, (1960)

28) R.T. Oakley, S.J. Rettig, N.L. Paddock, J. Trotter, *J. Am. Chem. Soc.*, 107, 6923, (1985)

29) H.R. Allcock, *Acc. Chem. Res.*, 12(10), 351, (1979); H.R. Allcock, W.D. Coggio, *Macromolecules*, 23, 1626, (1990)
30) L.G. Lund, N.L. Paddock, J.E. Proctor, H.T. Searle, *J. Chem. Soc.*, 2542, (1960)
31) H.R. Allcock, *Chem. Rev.*, 72(4), 328, (1972)
32) F.A. Cotton, A. Shaver, *Inorg. Chem.*, 10, 2362, (1971)
33) D.L. Herring, *Chem. Ind.*, (London), 717, (1960)
34) G.E. Coxon, D.B. Sowerby, *J. Chem. Soc.*, A, 1566, (1967)
35) R. Schmutzler, *Inorg. Syn.*, 9, 78, (1967); B. Green, D.B. Sowerby, *J. Chem. Soc., A*, 987, (1970); J. Chem. Soc., *Chem. Commun.*, 628, (1969)
36) G. Allen, C.J. Lewis, S.M. Todd, *Polymer*, 11, 31, (1970)
37) L.F. Audrieth, R. Steinman, A.D.F. Toy, *Chem. Rev.*, 32, 109, (1943); H.N. Stokes, *Am. Chem. J.*, 18, 629, (1896); *Am. Chem. J.*, 17, 275, (1895)
38) .Dishon, *J. Am. Chem. Soc.*, 71, 2251, (1949)
39) B.W. Fitzsimmons, R.A. Shaw, *J. Chem. Soc.*, 1735, (1964)
40) S.K. Ray, R.A. Shaw, *Chem. and Ind.*, 53, (1959)
41) R. Keat, R.A. Shaw, *J. Chem. Soc., London*, 2215, (1965)
42) S.K. Ray, R.A. Shaw, J. Chem. Soc., 872, (1961)
43) J. Emsley, N.L. Paddock, J. Chem. Soc., A, 2590, (1968)
44) C.W. Allen, *Chem. Rev.*, 91, 119, (1991); S.S. Krishnamurthy, A.C. Sau, M. Woods, *Adv. Inorg. Chem. and Radiochem.*, 21, 41, (1978)
45) S. Karthikeyan, S.S. Krishnamurthy, *Z. Anorg. Allgem. Chem.*, 513, 231, (1984); J.L. Schmutz, H.R. Allcock, *Inorg. Chem.*, 14, 2433, (1975)
46) M.-ul-Hasan, R.A. Shaw, M. Woods, *J. Chem. Soc., Dalton Trans.*, 2202, (1975)
47) K.V. Katti, S.S. Krishnamurthy, *J. Chem. Soc., Dalton Trans.*, 285, (1985)
48) K.D. Gallicano, R.T. Oakley, N.L. Paddock, R.D. Sharma, *Can. J. Chem.*, 59, 2654, (1981)
49) K.C. Kumara Swamy, M. Damodara Poojary, S.S. Krishnamurthy, H. Manohar, *J. Chem. Soc., Dalton Trans.*, 1881, (1985)
50) K.D. Gallicano, N.L. Paddock, *Can. J. Chem.*, 60, 521, (1982)
51) R.J. Richie, T.J. Fuller, H.R. Allcock, *Inorg. Chem.*, 19, 3842, (1980)
52) B. Thomas, G. Grossman, *Z. Anorg. Allgem. Chem.*, 448, 100, (1979); *ibid.*, pg. 107
53) K. Ramachandran, C.W. Allen, *J. Am. Chem. Soc.*, 104, 2396, (1982)
54) A.C. Chapman, D.H. Paine, H.T. Searle, D.R. Smith, R.F.M. White, *J. Chem. Soc., London*, 1768, (1961)
55) C.W. Allen, J.A. Mackay, *Inorg. Chem.*, 25, 4628, (1986)
56) K. Ramachandran, C.W. Allen, *Inorg. Chem.*, 22, 1445, (1983)

57) B. Capon, K. Hills, R.A. Shaw, *J. Chem. Soc.*, 4059, (1965); D.E. Brown, C.W. Allen, *Inorg. Chem.*, 26, 934, (1987)

58) Reference 11, Chapter 13

59) H.R. Allcock, J.L. Desorcie, L.J. Wagner, *Inorg. Chem.*, 24, 333, (1985)

60) S.N. Nabi, R.A. Shaw, C. Stratton, *J. Chem. Soc., Dalton Trans.*, 588, (1975); R. Keat, R.A. Shaw, *J. Chem. Soc.*, 4067, (1965)

61) B.W. Fitzsimmons, C. Hewlett, R.A. Shaw, *J. Chem. Soc.*, 4459, (1964)

62) N.L. Paddock, T.N. Ranganathan, S.M. Todd, *Can. J. Chem.*, 49, 164, (1971)

63) C.W. Allen, T. Moeller, *Inorg. Syn.*, 12, 293, (1970); C.W. Allen, A.J. White, *Inorg. Chem.*, 13, 1220, (1974); C.W. Allen, P.L. Toch, *Inorg. Chem.*, 20, 8, (1981)

64) P.J. Harris, C.L. Fadeley, *Inorg. Chem.*, 22, 561, (1983)

65) H. Winter, J.C. Van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1269, (1986)

66) P.J. Harris, J.L. Desorcie, H.R. Allcock, *J. Chem. Soc., Chem. Commun.*, 852, (1981); H.R. Allcock, J.L. Desorcie, P.J. Harris, *J. Am. Chem. Soc.*, 105, 2814, (1983)

67) M. Biddlestone, R.A. Shaw, *J. Chem. Soc, A*, 1750, (1970); C.W. Allen, R.L. Dieck, P. Brown, T. Moeller, C.D. Schmulbach, A.G. Cook, *J. Chem. Soc., Dalton Trans.*, 173, (1978)

68) J. Trotter, S.H. Whitlow, *J. Chem. Soc., A*, 455, (1970)

69) A.L. MacDonald, J. Trotter, *Can. J. Chem.*, 52, 734, (1974)

70) N.L. Paddock, T.N. Ranganathan, J.N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 1578, (1972)

71) H.R. Allcock, R.W. Allen, J.P. O'Brien, *J. Am. Chem. Soc.*, 99, 3984, (1977)

72) H.P. Calhoun, N.L. Paddock, J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2708, (1973)

73) J. Trotter, S.H. Whitlow, *J. Chem. Soc., A*, 460, (1970)

74) H.R. Allcock, E.C. Bissell, E.T. Shawl, *Inorg. Chem.*, 12, 2963, (1973)

75) H.R. Allcock, G.H. Riding, R.R. Whittle, *J. Am. Chem. Soc.*, 106, 5561, (1984); H.R. Allcock, L.J. Wagner, M.L. Levin, *J. Am. Chem. Soc.*, 105, 1321, (1983); P.R. Suszko, R.R. Whittle, H.R. Allcock, *J. Chem. Soc., Chem. Commun.*, 649, (1982)

76) P.P. Griegger, H.R. Allcock, *J. Am. Chem. Soc.*, 101, 2492, (1979); H.R. Allcock, P.P. Griegger, L.J. Wagner, M.Y. Bernheim, *Inorg. Chem.*, 20, 716, (1981)

77) H.R. Allcock, P.R. Suszko, L.J. Wagner, R.R. Whittle, B. Boso, *Organometallics*, 4, 446, (1985)

78) H.R. Allcock, P.J. Harris, *J. Am. Chem. Soc.*, 101, 6221, (1979)

79) W. Harrison, J. Trotter, *J. Chem. Soc., Dalton Trans.*, 61, (1973)

80) P.R. Suszko, R.R. Whittle, H.R. Allcock, *J. Chem. Soc., Chem. Commun.*, 960, (1980)

81) H.R. Allcock, K.D. Laviv, G.H. Riding, P.R. Suszko, R.R. Whittle, *J. Am. Chem. Soc.*, 106, 2337, (1984)
82) H.R. Allcock, P.P. Griegger, J.E. Gardner, J.L. Schmutz, *J. Am. Chem. Soc.*, 101, 606, (1979); H.R. Allcock, T.X. Neenan, B. Boso, *Inorg. Chem.*, 24, 2656, (1985)
83) H.R. Allcock, R.W. Allen, J.P. O'Brien, *J. Am. Chem. Soc.*, 99, 3987, (1977)
84) H.N. Stokes, *Am. Chem. J.*, 19, 782, (1897)
85) H. Staudinger, *Chem. Ber.*, 53, 1073, (1920)
86) K.H. Meyer, H. Mark, *Chem. Ber.*, 61, 1939, (1928)
87) K.H. Meyer, W. Lotmar, G.W. Pankow, *Helv. Chim. Acta.*, 19, 930, (1936)
88) H.R. Allcock, R.L. Kugel, *J. Am. Chem. Soc.*, 87, 4216, (1965)
89) H.R. Allcock, R.L. Kugel, *Inorg. Chem.*, 5, 1716, (1966)
90) H.R. Allcock, D.C. Ngo, M. Parvez, K. Visscher, *J. Chem. Soc., Dalton Trans.*, 1687, (1992)
91) H.R. Allcock, D.P. Mack, *J. Chem. Soc., Chem. Commun.*, 11, 685, (1970)
92) H.R. Allcock, C.T-W. Chu, *Macromolecules*,12, 551, (1979); H.R. Allcock, D.B. Patterson, T.L. Evans, *J. Am. Chem. Soc.*, 99, 6095, (1977)
93) H.R. Allcock, M.N. Mang, G.S. M°Donnell, M. Parvez, *Macromolecules*, 20, 2060, (1987)
94) H.R. Allcock, *Polymer*, 21, 673, (1980)
95) R.J. Ritchie, P.J. Harris, H.R. Allcock, *Macromolecules*, 12, 1014, (1979); H.R. Allcock, D.J. Brennan, B.S. Dunn, *Macromolecules*, 22, 1453, (1989)
96) H.R. Allcock, G.Y. Moore, *Macromolecules*, 8, 377, (1975)
97) I. Manners, G.H. Riding, J.A. Dodge, H.R. Allcock, *J. Am. Chem. Soc.*, 111, 3067, (1989)
98) H.R. Allcock, D.B. Patterson, *Inorg. Chem.*, 16, 197, (1977)
99) H.R. Allcock, K.D. Lavin, G.H. Riding, *Macromolecules*, 18, 1340, (1985)
100) J.O. Konecny, C.M. Douglas, *J. Polym. Sci*, 36, 195, (1959)
101) Reference 11, Chapter 15
102) J.R. Soulen, M.S. Silverman, *J. Polym. Sci.*, A1, 823, (1963)
103) J.O. Konecny, C.M. Douglas, M.Y. Gray, *J. Polym. Sci.*, 42, 383, (1960)
104) H.R. Allcock, R.J. Best, *Can. J. Chem.*, 42, 447, (1964)
105) H.R. Allcock, *Chem. Revs.*, 72(4), 349, (1972)
106) F.G.R. Gimblett, *J. Polym. Sci.*, 60, 529, (1962)
107) J.R. MacCallum, A. Werninck, *J. Polym. Sci.*, A1, 5, 3061, (1967)
108) J.R. MacCallum, J. Tanner, *J. Polym. Sci., B*, 7, 743, (1969)
109) P. Potin, R. DeJaeqer, *Eur. Polym. J.*, 27, 341, (1991); G. D'Halluin, R. DeJaeqer, J.P. Chambrette, P. Potin, *Macromolecules*, 25, 1254, (1992)

110) R.H. Neilson, P. Wisian-Neilson, *Chem. Rev.*, 88, 541, (1988); P. Wisian-Neilson, R. H.Neilson, *J. Am. Chem. Soc.*, 102, 2848, (1980)

111) R.H. Neilson, R. Hani, P. Wisian-Neilson, J.J. Meister, A.K. Roy, G.L. Hagnauer, *Macromolecules*, 20, 910, (1987)

112) P. Wisian-Neilson, R. Ford, *Phosphorus, Sulphur and Silicon*, 30, 315, (1987)

113) R.A. Montague, K. Matyjaszewski, *J. Am. Chem. Soc.*, 112, 67212, (1990); K. Matyjaszewski, M. Cypryk, J. Dauth, R. Montague, M. White, *Makromol. Chem., Macromol. Symp.*, 54/55, 13, (1992)

114) Reference 11, Chapter 16

115) H.R. Allcock, R.L. Kugel, G.F. Konopski, E.G. Stroh, *J. Chem. Soc., Chem. Commun.*, 985, (1970); E. Giglio, F. Pompa, A. Ripamonti, *J. Polym. Sci.*, 59, 293, (1962)

116) H.R. Allcock, M.S. Connolly, J.T. Sisko, S. Al-Shali, *Macromolecules*, 21, 323, (1988)

117) H.R. Allcock, W.J. Cook, D.P. Mack, *Inorg. Chem.*, 11, 2584, (1972)

118) R.J. Ciora Jr., J.H. Magill, *Macromolecules*, 23, 2350, (1990)

119) H.R. Allcock, M.L. Levin, P.E. Austin, *Inorg. Chem.*, 25, 2281, (1986); A.A. Dembek, C. Kim, H.R. Allcock, R.L.S. Devine, W.H. Steier, W. Spangler, *Chem. Mater.*, 2, 97, (1990)

120) H.R. Allcock, C. Kim, *Macromolecules*, 23, 3881, (1990)

121) H.R. Allcock, *J. Macromol. Sci., Rev. Macromol. Chem.*, 4, 3, (1970)

122) O. Schmitz-Dumont, *Z. Elektrochem.*, 45, 651, (1939)

123) J.K. Jacques, M.L. Mole, N.L. Paddock, *J. Chem. Soc.*, 2112, (1965)

124) F. Patat, P. Derst, *Angew. Chem.*, 71, 105, (1959); J.R. MacCallum, J. Tanner, *J. Macromol. Sci., Chem.*, 4, 481, (1970)

125) S.H. Rose, *J. Polym. Sci.*, B, 6, 837, (1968)

126) P.M. Blonsky, D.F. Schriver, P.E. Austin, H.R. Allcock, *J. Am. Chem. Soc.*, 106, 6854, (1984); D.F. Schriver, G.C. Farrington, *Chem and Eng. News*, 42, (1985); J.L. Bennett, A.A. Dembek, H.R. Allcock, B.J. Heyen, D.F. Schriver, *Chem. Mater.*, 1, 14, (1989)

127) H.R. Allcock, T.J. Fuller, *Macromolecules*, 13, 1338, (1980)

128) M.V. Lenton, B. Lewis, *J. Chem. Soc., A*, 665, (1966); G.R. Feistel, T. Moeller, *J. Inorg. Nucl. Chem.*, 20, 2731, (1967)

129) *Chem. and Eng. News*, 39, 63, (1961)

130) S.M. Zhivukhin, V.B. Tolstoguzov, V.V. Kireev, *Sov. Plast.*, 7, 24, (1963)

131) L.E.A. Godfrey, J.W. Schappel, *Ind. Eng. Chem. Prod. Res. Develop.*, 9, 426, (1970)

132) C.W. Allen, R.P. Bright, *Macromols*, 19, 571, (1986); K. Ramachandran, C.W. Allen, *Inorg. Chem.*, 22, 1445, (1983)

133) M.E. Fitzgerald, V. Griffing, J. Sullivan, *J. Chem. Phys.*, 25, 926, (1956)

134) J. Curie, P. Curie, *Compt. Rend*, 91, 294, (1880); J. Curie, P. Curie, *Compt. Rend.*, 93, 1137, (1881)

135) M.A. Margulis, *Ultrasonics*, 157, (1985)

136) B.E. Noltingk, E.A. Neppiras, *Proc. Phys. Soc.*, 63B, 674, (1950)

137) K.S. Suslick, *Science*, 253, 1397, (1991)

138) F.D. Smith, *Philos. Mag.*, 19, 1147, (1935)

139) L. Bergmann, *'Ultrasonics'*, G. Bell and Sons, New York, (1964)

140)M.E. Fitzgerald, V. Griffing, J. Sullivan, *J. Chem. Phys.*, 25, 926, (1956)

141) H.G. Flynn, *Physical Acouctics*, 1B, 57, (1964)

142) H.J. Eyring, *J. Chem. Phys.*, 4, 283, (1936)

143) W. Gaertner, *J. Acoust. Soc. Am.*, 26, 977, (1954)

144) E.A. Neppiras, B.E. Noltingk, *Proc. Phys. Soc.*, 64B, 1032, (1951)

145) A.W. Brett, H.H.G. Jellinek, *J. Polym. Sci.*, 13, 441, (1954)

146) L.A. Crumm, *Appl.Sci. Res.*, 38, 101, (1982)

147) K.S. Suslick, R.E.Johnson, *J. Am. Chem. Soc.*, 106, 6856, (1984); C. Petrier, A. Jeunet, J-L. Luche, G. Reverdy, *J. Am. Chem. Soc.*, 114, 3148, (1992)

148) A. Tuulmets, K. Kaubi, K. Heinoja, *Ultrasonics Sonochemistry*, 2(2), 75, (1995)

149) C. Hubert,A. Munoz, B. Carrigues, J.-L. Luche, *J. Org. Chem.*, 60, 1488, (1995)

150) T.J. Mason, J. Lindley, *Chem. Rev.*, 16, 275, (1989)

151) K.S. Suslick, D.J. Casadonte, M.L.H. Green, *Ultrasonics*, 25, 26, (1987)

152) T.J. Mason, J.P. Lorimer, *'Sonochemistry - Theory, Applications and Uses of Ultrasound in Chemistry'*, Ellis Horwood Limited, (1988), Chapter 1

153) H.W. Melville, A.J. Murray, *Trans. Faraday. Soc.*, 46, 996, (1950)

154) E.W. Flosdorf, L.A. Chambers, *J. Am. Chem. Soc.*, 55, 3051, (1933); A.S. Gyorgi, *Nature*, 131, 279, (1933)

155) F. Brohult, *Nature*, 140, 805, (1937)

156) G. Schmid, O. Rommel, *Z. Electrochem.*, 45, 659, (1936)

157) G.J. Price, *Advances in Sonochemistry*, 1, 231, (1990)

158) H.H.G. Jellinek, G. White, *J. Polym. Sci.*, 6, 757, (1951)

159) G. Schmid, C. Schneider, A. Henglein, *Kolloid. Z.*, 148, 73, (1956)

160) M.T. Shaw, F. Rodriguez, *J. Appl. Polym. Sci.*, 11, 335, (1967)

161) T.G. Schoon, G. Rieber, *Angew. Makromol. Chem.*, 23, 43, (1972); S.L. Malhotra, *J. Macromol. Sci., Chem.*, A23, 729, (1986)

162) G. Gooberman, J. Lamb, *J. Polym. Sci.*, 47, 229, (1960)

163) G. Gooberman, J. Lamb, *J. Polym.* Sci., 42, 35, (1960)
164) W.B. Smith, H.W. Temple, *J. Phys. Chem.*, 72, 4613, (1968)
165) M.A.K. Mostafa, *J. Polym. Sci.*, 33, 311, (1958)
166) H.H.G. Jellinek, *J. Polym. Sci.*, 37, 485, (1959)
167) M.A.K. Mostafa, *J. Polym. Sci.*, 28,519, (1958)
168) M. Okuyama, *Z. Elektrochem.*, 59, 565, (1955)
169) G.J. Price, P.F. Smith, *Polymer*, 34, 4111, (1993)
170) G. Schmid, E. Beutenmuller, *Z. Elektrochem.*, 49, 325, (1943)
171) S.V. Golubev, Z.A. Tikhonova, Y.D. Semchikov, I.V. Trubina, *Vyskomol. Soedin. Ser. A.*, 29, 2393; [CA108(4):22407]
172) S.L. Malhotra, *J. Macromol. Sci., Chem.*, A17, 601, (1982); A.M. Basedow, K.H. Ebert, E. Fosshag, *Makromol. Chem.*, 179, 2565, (1978)
173) B.B. Thomas, W.J. Alexander, *J. Polym. Sci.*, 25, 285, (1957)
174) G. Schmid, E. Beutenmuller, *Z. Elektrochem.*, 50, 209, (1940)
175) H.H.G. Jellinek, H.W. Brett, *J. Polym. Sci.*, 21, 535, (1956)
176) P.F. Smith, PhD Thesis, University of Bath, (1991)
177) M.A.K. Mostafa, *J. Polym. Sci.*, 33, 295, (1958)
178) P.J. West, PhD. Thesis, University of Bath, (1993)
179) M.V. Encina, E. Lissi, M. Sarasua, L. Gargallo, D. Radic, *J. Polym. Sci., Polym. Lett.*, 18, 757, (1980)
180) G. Schmid, *Physik. Z.*, 41, 326, (1940)
181) H.H.G. Jellinek, G. White, *J. Polym. Sci.*, 7, 21, (1951)
182) A. Thieme, *Physik. Z.*, 39, 384, (1938)
183) G.R. Thomas, *J. Phys. Chem.*, 63, 1725, (1959)
184) G. Gooberman, *J. Polym. Sci.*, 42, 25, (1960)
185) J.A. Odell, A.Keller, *Polym. Sci., Polym. Phys. Ed.*, 24, 1889, (1986); A.J. Muller, J.A. Odell, A. Keller, *Polymer Commun.*, 30, 298, (1989)
186) R.E. Harrington, B.H Zimm, *J. Phys. Chem.*, 69, 161, (1965)
187) A. Henglein, *Makromol. Chem.*, 15, 188, (1955)
188) M. Tabata, T. Miyazawa, J. Sohma, O. Kobayashi, *Chem. Phys. Lett.*, 73, 178, (1980)
189) J.R. Thomas, D.L. DeVries, *J. Phys. Chem.*, 63, 254, (1959)
190) A.N. Mujumdar, S.G. Young, R.L. Merker, J.H. Magill, *Macromols.*, 23, 14, (1990)
191) M. Biddlestone, R.A. Shaw, *J. Chem. Soc. A.*, 178, (1969)
192) F. Heatley, S.M. Todd, *J. Chem. Soc. A.*, 1152, (1966)
193) R.A. Shaw, *J. Organomet. Chem.*, 341, 357, (1988)

194) B.W. Fitzsimmons, C. Hewlett, K. Hills, R.A. Shaw, *J.Chem. Soc. A.*, 679, (1967)

195) K.S. Dhathathreyan, S.S. Krishnamurthy, A.R. Vasudevamurthy, R.A. Shaw, M. Woods, *J. Chem. Soc., Dalton Trans.*, 1549, (1982)

196) P.E. Austin, G.H. Riding, H.R. Allcock, *Macromols.*, 16, 719, (1983)

197) T. Hokelek, Z. Kilic, A. Kilic, *Acta. Cryst.*, C50, 453, (1994)

198) P.J. Harris, H.R. Allcock, *J. Am. Chem. Soc.*, 100, 6512, (1978)

199) H.R. Allcock, M.S. Connolly, P.J. Harris, *J. Am. Chem. Soc.*, 104, 2482,(1982)

200) A.P. Carroll, R.A. Shaw, *J. Chem. Soc. A.*, 914, (1966)

201) H. Bredereck, R. Gompper, K. Klemm, H. Rempfer, *Chem. Ber.*, 92, 837, (1959); F. Cramer, M. Winter, *Chem. Ber.*, 94, 989, (1961)

202) J.C. Graham, D.H. Marr, *Can. J. Chem.*, 50, 3857, (1972)

203) A. Streitweiser,C.H. Heathcock, *'Introduction to Organic Chemistry'*, 3rd Edtn., Macmillan, (1985), Chapter 23

204) *'Vogels Textbook of Practical Organic Chemistry'*, 4th Edtn., ed. B.S. Furniss, Longman, (1978)

205) H.R. Allcock, *Chem. Mater.*, 6, 1476, (1994); S. Cohen, M. Carmen Bano, K.B. Visscher, M. Chow, H.R. Allcock, R. Langer, *J. Am. Chem. Soc.*, 112, 7832, (1990); H.R. Allcock, J.Y. Chang, *Macromols.*, 24, 993, (1991)

206) H.A. Al-Madfa, R.A. Shaw, *Phosphorus, Sulphur and Silicon*, 45, 1, (1989)

207) S.R. Contractor, M.B. Hursthouse, L.S. Shaw, (nee Gozen), R.A Shaw, H. Yilmaz, *Acta. Cryst.*, B41, 122, (1985)

208) A.H. Alkubaisi, H.G. Parkes, R.A. Shaw, *Heterocycles*, 28, 347, (1989); A.H. Alkubaisi, R.A. Shaw, *Phosphorus, Sulphur and Silicon*, 55, 49, (1991)

209) S.R. Sandler, F.R. Berg, *J. Polym. Sci., A-1*, 4, 1253, (1966)

210) E.J. Vandenberg, *J. Polym. Sci., Polym. Chem.*, 23, 915, (1985)

211) R. Tokar, P. Kubisa, S. Penczek, A. Dworak, *Macromols.*, 27, 320, (1994)

212) J.-L. Luche, C. Einhorn, J. Einhorn, J.V. Sinisterra-Gago, *Tett. Lett.*, 31(29), 4125, (1990)

213) I. Manners, W.D. Coggio, M.N. Mang, M. Parvez, H.R. Allcock, *J. Am. Chem. Soc.*, 111, 3481, (1989)

214) F.A. Cotton, G. Wilkinson, *'Advanced Inorganic Chemistry'*, 5th Edtn., Wiley Interscience, (1988), Chapter 5

215) Ch. Elschenbroich, A. Salzer, *'Organometallics, A Concise Introduction'*, 2nd Edtn., VCH Publishers, (1992), Chapter 4.

216) H.R. Allcock, P.J. Harris, L. Nissan, *J. Am. Chem. Soc.*, 103, 2256, (1981)

217) G.J. Price in *'Current Trends in Sonochemistry'*, Royal Society of Chemistry, Cambridge, (1992)

218) Y. Shen, K. Shen, Q. Wang, H. Xu, X.J Xu, *Macromol. Sci. Chem.*, A23, 141, (1986)

219) R.H Neilson, R. Hani, P. Wissian-Neilson, J.S Meister, A.K. Roy, G.L Hagnauer, *Macromolecules.*, 20, 910, (1987)

220) H.R Allcock, W.J. Cook, *Macromolecules.*, 3, 284, (1974)

221) M. Zeldin, W.J. Jo, E.M. Pearce, *Macromolecules.*, 13, 1163, (1980)

222) S.V. Peddada, J.H. Magill, *Macromolecules.*, 16, 1258, (19830

223) V.S. Papkov, M.N. Il'ina, D.R. Tur, G.L. Slominskii, *Polym. Sci. USSR*, 31, 2509, (1989)

224) M.L. White, K. Matyjaszewski, *J. Macromol. Sci., Pure and Applied Chem.*, A32, 1115, (1995)

225) H. Hiraoko, W-Y. Lee, L.W. Welsh, R.W. Allen, *Macromolecules.*, 12, 753, (1979)

226) J.P. O'Brien, W.T. Ferrar, H.R. Allcock, *Macromolecules.*, 12, 108, (1979)

227) G.Z. Schmid, *Phys. Chem.*, 186, 113, (1940)

228) D.W. Ovenall, G.W. Hastings, P.E.M. Allen, *J. Polym. Sci.*, 33, 207, (1958)

229) B.S. El'tsefon, A.A. Berlin, *Polym. Sci. USSR*, 5, 668, (1964)

230) T. Sato, D.E. Nalepa, *J. Appl. Polym. Sci.*, 22, 865, (1978)

231) H.H.G. Jellinek, *'Degradation of Vinyl Polymers'*, Academic Press, New York, (1955)

232) G.J. Price, M.P. Hearn, E.N.K. Wallace, A.M. Patel, *Polymer*, 37(12), 2203, (1996)

233) T.J. Mason in CRAC 28, *'Chemistry with Ultrasound'*,ED. T.J. Mason, Elsevier Applied Science, (1990)

234) C.W. Allen, I.C. Paul, T. Moeller, *J. Am. Chem. Soc.*, 89, 6362, (1967)

235) N.V. Mani, A.J. Wagner, *Acta. Cryst.*, B27, 51, (1971)

236) H.R. Allcock, J.A. Dodge, L.S. Van Dyke, C.R. Martin, *Chem. Mater.*, 4, 780, (1992)

237) M. Pomerantz, G. Krishnan, M.W. Victor, C. Wei, K. Rajeshwar, *Chem. Mater.*, 5, 705, (1993)

238) H.R. Allcock, K.B. Visscher, I. Manners, *Chem. Mater.*, 4, 1188, (1992)

239) H.R. Allcock, R.J. Fitzpatrick, L. Salvati, *Chem. Mater.*, 4, 769, (1992)

240) B. Grushkin, M.G. Sanchez, R.G. Rice, *Inorg. Chem.*, 3, 623, (1964)

241) C.W Allen, F.Y. Tsang, T. Moeller, *Inorg. Chem.*, 7, 2183, (1968)

242) B. Grushkin, M.G. Sanchez, M.V. Ernest, J.L. McClanahan, G.E. Ashby, R.G. Rice, *Inorg. Chem.*, 4, 1538, (1965)

243) J. Reuben, *Magn. Reson. Chem.*, 25, 1049, (1987)

244) H.P. Latscha, Z. Anorg. *Allgem. Chem.*, 362, 7, (1968)

245) S.S. Krishnamurthy, M. Woods, *Annu. Rep. NMR Spectros.*, 19, 1, (1987)

246) C.W. Allen, T. Moeller, *Inorg. Chem.*, 7, 2177, (1968)

247) E.D. Becker, *'High Resolution NMR'*, Academic Press, New York, (1969)